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TIME-SETTLEMENT BEHAVIOR OF PROCESSED REFUSE

Part III - Anaerobic Digestion of Milled Refuse

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16. ABSTRACT

The objectives of this laboratory investigation were to gain an understanding of the decomposition of milled refuse under anaerobic conditions, the rates of decomposition, and the gas production and composition. The rates of decomposition of cellulose and cellulosic materials, gas production per unit weight of materials digested and the CH_4 to CO_2 ratios were obtained from the literature for different systems. Similar data from laboratory experiments on the anaerobic decomposition of milled refuse were analyzed and compared with the information obtained from the literature. The rate constant decomposition, k_e at 37°C, reported in the literature for the different systems, varied from 3.3×10^{-5} to 1.97 day^{-1}. Gas production ranged from near zero to 14 ft^3 per pound of volatile matter digested and the CH_4 to CO_2 ratio varied between 0.3 and 1.86. For anaerobic digestion of milled refuse in the laboratory experiments, the rate constant (normalized to 37°C) for the reduction of volatile matter varied between 0.00105 and 0.00216 day^{-1}. The low rates were observed for the digesters which were either seeded with a non-acclimatized culture or not seeded at all. Gas production ranged from 6.9 to 12.8 ft^3/lb of volatile matter digested. The averaged CH_4 to CO_2 ratio, for the initial phase of gas production, varied from 0.13 to 1.09, the lowest ratio being observed for the digester which was operated at the lowest temperature, 20°C.

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

The report provides information on decomposition rates, gas production values, and composition ratios for an anaerobic sanitary landfill containing milled municipal refuse. Data from laboratory experiments are compared with the range of values obtained in a literature search.

Francis T. Mayo
Director
Municipal Environmental Research
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ABSTRACT

Sanitary landfilling is the most popular method for the final disposal of municipal solid wastes. Due to the limited number of sites available for use as landfills, a need exists for improved methods of sanitary landfilling. Milling of refuse prior to landfilling appears to have several advantages over conventional sanitary landfills. The objectives of this investigation were to gain an understanding of the decomposition of milled refuse under anaerobic conditions, the rates of decomposition, and the gas production and composition.

The rates of decomposition of cellulose and cellulosic materials, gas production per unit weight of materials digested and the CH_4 to CO_2 ratios were obtained from the literature for different systems. Similar data from laboratory experiments on the anaerobic decomposition of milled refuse were analyzed and compared with the information obtained from the literature. The rate constant decomposition, k_e at 37°C, reported in the literature for the different systems, varied from 3.3×10^{-5} to 1.97 day^{-1}. Gas production ranged from near zero to 14 ft^3 per pound of volatile matter digested and the CH_4 to CO_2 ratio varied between 0.03 and 1.86.

For anaerobic digestion of milled refuse in the laboratory experiments, the rate constant (normalized to 37°C) for the reduction of volatile matter varied between 0.00105 and 0.00216 day^{-1}. The low rates were observed for the digesters which were either seeded with a non-acclimatized culture or not seeded at all. Gas production ranged from 6.9 to 12.8 ft^3/lb of volatile matter digested. The averaged CH_4 to CO_2 ratio, for the initial phase of gas production, varied from 0.13 to 1.09, the lowest ratio being observed for the digester which was operated at the lowest temperature, 20°C.

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INTRODUCTION

One of the complications of the rapid urbanization and the high standard of living in the United States is the associated increase in the amount of municipal solid wastes produced in a community. An efficient refuse collection and disposal system is essential to the maintainence of a safe and attractive environment in a community.

At present the production of municipal solid wastes in the United States is in excess of 300 billion pounds annually. Currently, the final disposal of solid wastes is accomplished through the use of sanitary landfills, incineration, composting and/or salvage and recycling. Of these disposal methods, the sanitary landfill is, by far, the most popular; however, frequently, they are not operated in compliance with the legal, public health and aesthetic requirements. Also, the number of sites available for use as sanitary landfills are limited and their capacities are being depleted rapidly. A need therefore exists for improved methods of operating sanitary landfills. Promising studies have been conducted on bailing or milling of municipal solid wastes.

A demonstration grant project investigating milling as an auxilary process in connection with sanitary landfilling has been completed at Madison, Wisconsin, under the auspices of the U. S. EPA and the City (1). Only household refuse was involved in this project. The study has shown that the process

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may have advantages from certain standpoints and that it may have a definite place under some circumstances.

Approximately 70% of municipal solid wastes are cellulosic material (on a dry weight basis). Depending upon the environmental conditions, a certain portion of this material decomposes anaerobically within a landfill by microbial action, the principal end products being carbon dioxide, methane, organic acids and water.

The objectives of this study are to gain an understanding of the decomposition process, the rates of decomposition, the gas production, and composition under anaerobic conditions.

A literature search was conducted to obtain the following information.

1. A model for the decomposition of cellulosic materials, decomposition rates, gas quantities and composition, and the intermediate products.
2. Ranges of decomposition rates and gas quantities produced, applicable for the decomposition of cellulosic materials, in various processes.
3. The governing steps or factors effecting the decomposition rates, gas production, gas composition, and the intermediate products.

Data from laboratory experiments (2) were analyzed and the rates of decomposition, gas production and gas composition were calculated and discussed with reference to the information obtained from the literature search.

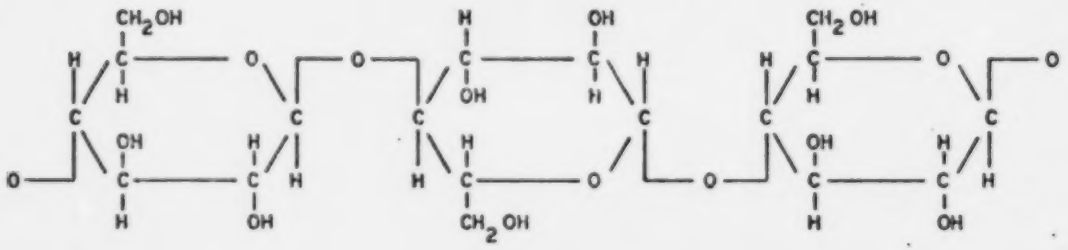
The information gained from this study may help in

predicting the maximum decomposition rate and gas production that may be encountered in sanitary landfills of milled refuse.

MICROBIAL DECOMPOSITION OF CELLULOSE AND CELLULOSIC MATERIALS

Structure

Cellulose is a high molecular weight (approximately 500,000 gm/mole) polymer of β-1,4-linked D-glucose residues. Its empirical formula is $(C_6H_{10}O_5)_n$. A portion of the cellulose molecule is as follows:



Cellulose, as found in nature, has a complex structure. Cowling (3) describes, "Native cellulose is an aggregate of well defined partly crystalline microfibrils of indefinite length. Within each microfibrils, the linear molecules of cellulose are bound laterally by hydrogen bonds and van der Waals forces into a linear [although a larger complex] partially crystalline structure. The cellulose molecules are associated in various degrees of parallelism. Regions of a high degree of order are called crystallites or micelles, those in which the cellulose is more randomly oriented are called amorphous or paracrystalline regions. These crystalline and amorphous regions are interspersed with one another and are

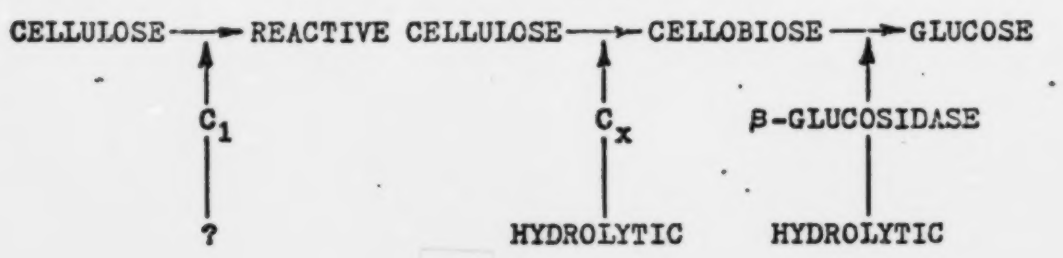
not discrete or uniform in size; the cellulose molecules grade gradually from the crystalline to the amorphous phase. The cellulose molecules are in general much longer than individual crystallites. They cellulose molecules therefore traverse consist of several crystalline and amorphous regions."

Norkrans (4) states, "Native cellulose is not simply a glucose anhydride chain, showing a characteristic insolubility in water at even very short chain lengths, but a high [molecular weight] polymer arranged in supramolecular structures, laid down in cells and tissues and embedded in a noncellulosic matrix, often surrounded by lignin."

These structural features complicate the understanding of the degradation process.

Enzymatic Degradation of Cellulose

Cellulose is insoluble in water and can not permeate cell membranes, cellulolytic organisms must possess an enzyme system capable of synthesizing a soluble product from cellulose. Enzymes which hydrolyze cellulose are broadly defined as cellulases. Microbial cellulase has been supposed to be extracellular. The mode of action of cellulases has been described by Mandels and Reese (5) as a C_1 and C_x (an enzyme system) concept in the following schematic way:



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Mandels and Reese assume C_1 to act in a way to permit an increased moisture uptake, hydrating the cellulose and pushing apart the closely packed chains, to make the linkages accessible for the action of the hydrolytic β-1,4-endoglucanase (C_x). The hydrolytic C_x is able to attac all celluloses, ranging from soluble cellulose derivatives to celluloses swollen by alkali or acids or by means of mechanical treatment such as grinding.

Li et al (6) maintain that the key property of the C_1 component of the enzyme system is its capacity to attack highly crystalline cellulose. They have been able to separate the enzyme system in to different components with distinct enzymatic properties. The components are hydrocellulase, endoglucanase, and exoglucanase.

Hydrocellulase corresponds to the C_1 component, being the only one having the capacity to attack crystalline cellulose at any appriciable rate. The primary product is cellobiose.

Endoglucanase behaves as a typical C_x enzyme. Random attack on relatively long chains of amorphous cellulose is assigned to this enzyme.

Exoglucanase completes the hydrolysis of cellulose to glucose, using the products obtained both from the action of the hydrocellulase and the endoglucanase.

The degradation of native cellulose by enzymes or microorganisms is a relatively slow process as only a small fraction of the linkages are accessible to an enzyme at any given time. The kinetics of the process is complicated and have

not received extensive attention.

Two modes of enzymatic attack on cellulose have been proposed. They are, endwise removal of successive glucosyl moieties and completely random attack on all glucosidic bonds. In the first instance only one bond, the terminal bond, is susceptible to enzymatic attack. In the second, all bonds are equally susceptible.

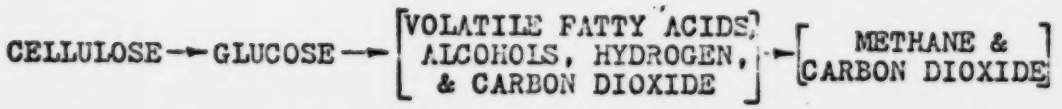
The susceptibility of cellulose to hydrolysis by cellulases depends mainly on its accessibility to the extracellular enzymes secreted by or bound on the surface of the cellulolytic microorganisms. Direct physical contact between the enzymes and the cellulosic substrate molecules is essential for hydrolysis. Since cellulose is an insoluble and structurally complex substrate, this contact can be achieved only by diffusion of the enzymes from the organisms into the complex structural matrix of the cellulose. Any structural feature that limits the accessibility of the cellulose to enzymes by diffusion within the fiber will diminish the susceptibility of the cellulose of that fiber to microbial degradation (3).

Culture conditions are of great importance for cellulase production by microorganisms. Apparently insignificant differences in the conditions may influence not only the quantity of enzymes produced but even the quality. Composition of the culture medium (quantity and quality of the cellulose used, the amount of metal salts present), pH, temperature, and the oxygen supply, are some of the major factors influencing cellulase production (4).

Most cellulolytic organisms are found among bacteria and fungi. In more or less anaerobic, closed environments, bacteria are the outstanding cellulose decomposers. Anaerobic eubacterial cellulose decomposers are also to be found in soil, in addition to aerobic species belonging mainly to the genera Cellvibrio and Cellulomonas. Furthermore, some actinomycetes and myxobacteria, including the imperfect genera Sporocytophaga and Cytophaga, are known as strong cellulose decomposers in soil.

Anaerobic Decomposition of Cellulosic Materials

Under anaerobic conditions, as in landfills, sludge digesters, and in the rumen of herbivores, cellulosic materials are decomposed by anaerobic bacteria in the presence of water. The end products are carbon dioxide and methane. Several different groups of bacteria are involved in the decomposition process. A brief schematic representation of the process is shown below.



In the first stage, a certain specific group of cellulolytic bacteria (4,7,8,9) are involved which are capable of using cellulose as a carbon source. These bacteria hydrolyze

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cellulose enzymatically to glucose and then to volatile fatty acids and alcohols. Several species of anaerobic facultative bacteria, collectively known as the "acid formers" are able to use glucose as a substrate and produce the volatile fatty acids and alcohols.

In the second stage, a group of strictly anaerobic bacteria (9,11,12), generally known as the "methane formers", are responsible for the breakdown of the volatile fatty acids and alcohols with the production of methane and carbon dioxide. Schematic diagrams of the two stages of the microbial, anaerobic decomposition of cellulose are shown in Figs. 1 and 2.

In any system the total production of methane and carbon dioxide is dependent on the distribution and the relative preponderance of the different species of microorganisms involved, which in turn, is dependent on the culture medium and the environmental conditions.

Chemistry of Decomposition of Cellulose

As seen in the previous section, the anaerobic decomposition of cellulose involves, the hydrolysis of cellulose to glucose, the fermentation of glucose to volatile fatty acids and alcohols, and finally the fermentation of these intermediate products to methane. The overall reactions associated with the different pathways of decomposition of cellulose by microorganisms are as follows (9,10,11,12,13).

Hydrolysis

$$(C_6H_{10}O_5)_n + n\ H_2O \rightarrow n\ C_6H_{12}O_6 \qquad \ldots 1$$

Acid Fermentations

Glycolysis:

$$C_6H_{12}O_6 \rightarrow 2\ CH_3CHOHCOOH \quad ...2$$

Alcoholic fermentation:

$$C_6H_{12}O_6 \rightarrow 2\ CH_3CH_2OH + 2\ CO_2 \quad ...3$$

Mixed fermentations:

$$C_6H_{12}O_6 \rightarrow CH_3CHOHCOOH + CH_3CH_2OH + CO_2 \quad ...4$$

$$2\ C_6H_{12}O_6 \rightarrow 3\ CH_3COOH + 2\ CH_3CHOHCOOH \quad ...5$$

$$2\ C_6H_{12}O_6 + 4\ H_2O \rightarrow CH_3CH_2CH_2COOH + CH_3COOH + 6\ CO_2 + 10\ H_2 \quad ...6$$

$$2\ C_6H_{12}O_6 + H_2O \rightarrow CH_3COOH + 2\ CH_3CHOHCOOH + CH_3CH_2OH + 2\ CO_2 + 2\ H_2 \quad ...7$$

Formic acid fermentation of pyruvic acid:

$$CH_3COCOOH + 3\ H_2O \rightarrow 3\ HCOOH + 2\ H_2 \quad ...8$$

Acetic acid fermentation of pyruvic acid:

$$CH_3COCOOH + H_2O \rightarrow CH_3COOH + CO_2 + H_2 \quad ...9$$

Butyric acid fermentation of pyruvic acid:

$$CH_3COCOOH + 5\ H_2 \rightarrow 3\ CH_3CH_2CH_2COOH + 3\ H_2O + 3\ CO_2 \quad ..10$$

Propionic acid fermentation of lactic acid:

$$3\ CH_3CHOHCOOH \rightarrow 3\ CH_3CH_2COOH + CH_3COOH + CO_2 + H_2O \quad ..11$$

Decomposition of propionic acid:

$$CH_3CH_2COOH + H_2O \rightarrow HCOOH + CH_3CH_2OH \quad ..12$$

Decomposition of formic acid:

$$HCOOH \rightarrow CO_2 + H_2 \quad ..13$$

Methane Fermentations

$$4\ HCOOH \rightarrow CH_4 + 3\ CO_2 + 2\ H_2O \quad ..14$$

$CH_3COOH \rightarrow CH_4 + CO_2$ ..15

$2\ CH_3CH_2CH_2COOH + CO_2 + 2\ H_2O \rightarrow CH_4 + 4\ CH_3COOH$ ..16

$2\ CH_3CH_2OH + CO_2 \rightarrow CH_4 + 2\ CH_3COOH$ ..17

$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$ ..18

The CH_4/CO_2 Ratio for Different Methane Fermentation Pathways

When cellulose is completely decomposed to methane and carbon dioxide by any one of the nine acid fermentation pathways and the corrosponding methane fermentation pathways, the CH_4 to CO_2 ratio is equal to one. Therefore the CH_4 to CO_2 ratio is always one irrespective of distribution of cellulose decomposition among the nine different pathways of acid fermentation.

Case A: Assuming complete breakdown of cellulose by "acid formers" as shown in Fig. 1, and an uniform and equal distribution of cellulose decomposition amongst the different pathways, the overall chemical equation is as follows:

270 Cellulose + 599 $H_2O \rightarrow$ 185 Acetic + 51 Butyric
+ 205 Ethanol + 636 CO_2 + 760 H_2

On further degradation by the "methane formers", assuming that the reaction goes to completion, we obtain:

270 Cellulose + 270 $H_2O \rightarrow$ 810 CH_4 + 810 CO_2

Case B: Using the same assumptions as in Case A, except that the formic acid formed during acid fermentation is not broken down to carbon dioxide and hydrogen, we have:

270 Cellulose + 599 $H_2O \rightarrow$ 280 Formic + 185 Acetic + 51 Butyric
+ 205 Ethanol + 356 CO_2 + 480 H_2

which again on completion of the methane fermentation gives:

$270\ \text{Cellulose} + 270\ H_2O \rightarrow 810\ CH_4 + 810\ CO_2$

The effect on the CH_4 to CO_2 ratio when the different methane fermentation pathways are not available, have been evaluated for the cases A and B. It is assumed that when a certain pathway is available, the reaction goes to completion. The results are summarized in Table 1. The methane fermentation pathways available have been designated by equation numbers. The total quantites of methane and carbon dioxide formed for the decomposition of 270 molecules of cellulose and the calculated CH_4 to CO_2 ratios, for different combinations of available methane fermentation pathways, have been shown for cases A and B.

The calculated CH_4 to CO_2 ratios will be lower when the available methane fermentation pathways are not completely effective, i.e., only a certain percentage of a particular intermediate product is broken down by the "methane formers".

Therefore, the CH_4 to CO_2 ratio for cellulose decomposition may vary from zero to one, depending upon the efficiency of the methane fermentation pathways, but will not exceed one.

Rates of Decomposition of Cellulosic Materials

The information, on the rates of decomposition and the quantity and composition of the gases produced, obtained from the literature, is summarized in this section. The decomposition of cellulosic materials by microorganisms within different systems (anaerobic and aerobic) have been studied so as to obtain the ranges of rates and gas quantities for

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various processes.

Rates of decomposition of cellulose and cellulosic materials have been calculated for the different digestion processes (8,10,14,17,18,19) using,

$$y = y_o e^{-kt}$$

where, y = concentration of cellulose, volatile solids or the total carbon content in the system at time, t

y_o = initial concentration of cellulose, volatile matter or the carbon content in the system

k = rate constant, day^{-1}

t = time, days

The calculated rate constants have been normalized to 37 °C according to the equation (20),

$$\frac{k}{k_o} = e^{\frac{E}{R}\frac{T - T_o}{TT_o}}$$

where, k = rate constant at T °K

k_o = rate constant at T_o °K

E = activation energy, $\frac{cal}{gm\ mole\text{-}^oK}$

R = gas constant = 1.99 $\frac{cal}{gm\ mole\text{-}^oK}$

T & T_o in °Kelvin

It was assumed that the activation energy, E, for cellulosic materials were similar to those for sewage solids and

its values were estimated on the basis of a study by Fair and Moore (21). Values of the activation energy used were, 4900 cal/gm mole-°K when the rate constants at 20 °C and 34 °C were normalized to 37 °C and 3000 cal/gm mole-°K when the rate constants at 55 °C were normalized to 37 °C.

The Rumen

Cellulosic materials are easily digested by ruminants. Anaerobic, cellulolytic bacteria within the rumen decompose cellulose to volatile fatty acids, carbon dioxide and methane. Hungate (7) reported the overall equation to represent the fermentation of carbohydrates, calculated on the basis of the average ratios in which acetic, propionic, and butyric acids are produced, as follows.

58 Hexose ⟶ 62 Acetic + 22 Propionic + 16 Butyric
+ $60\frac{1}{2}$ CO_2 + $33\frac{1}{2}$ CH_4 + 27 H_2O

From the above equation the gas production by ruminants is estimated at 3.59 ft^3/lb of cellulose digested with a CH_4 to CO_2 ratio of 0.55. The volatile fatty acids produced in the rumen are almost completely absorbed by the animal and are metabolizied in the liver. The gas produced per pound of cellulose actually converted to carbon dioxide and methane is 13.3 ft^3.

The quantity of methane produced by a non-fistulated cow placed in a special metabolism chamber was measured. The animal produced 0.28 moles of methane per 100 gm cellulose digested per day, equivalent to 1 ft^3/lb of cellulose digested.

Sanitary Landfills

In a study (14) by the State Water Quality Control Board, California, movements of gases produced by decomposing refuse were studied in an experimental landfill. Domestic refuse, totalling 4290 tons, was placed in three 6 ft layers, each separated by a 6 to 10 inch layer of silt. The landfill was covered with a 16 inch layer of silt. The depth of the landfill varied from 18 to 25 ft. The refuse density, in place, was estimated at approximately 400 lbs per cubic yard (water content, 17.4%).

Observations were made over a period of two and a half years. The temperature within the landfill varied from 16 °C to 37 °C, while the water content, with respect to the dry refuse weight, was between 141% and 252%. Some aerobic activity was suspected in the top layer while the two bottom layers were essentially anaerobic.

The CO_2 concentration in the gas produced was usually in the 60 to 70% range; a maximum of 89.4% was reported. The CH_4 concentration varied from nil in the top layer to about 20% in the bottom layer. A maximum of 29.6% was observed.

From the estimated average rates of gas production in the landfill, the CH_4 to CO_2 ratio was 0.063 during the first two month period and increased to 0.151 at the end of the two and a half year period.

The half life of the landfill was estimated at 57 years considering carbon loss by gasification only.

The total volume of gas produced during the first 750

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days was estimated at 394.4 ft^3/cubic yard of refuse or 1.13 ft^3/lb of dry refuse.

In a study by Merz and Stone (15) 31,000 lbs of refuse with an initial water content of 69.9% (dry weight basis) was sealed in a steel tank and the quantities of gas generated were measured. Approximately 40 ft^3 of gas was produced within the first three days after which gas production fell off to negligible quantities. The addition of 450 gallons of water on the 62nd. day brought the water content to an estimated 90.6%. Gas production resumed in measurable quantities after the 230th. day. A total of 2025 ft^3 of gas was measured until the 750th. day after which gas production was again negligible. The total gas production reported was only 41.64 ft^3/cubic yard of refuse or 0.11 ft^3/lb of dry refuse.

Merz and Stone (16) reported composition of gases evolved in five experimental landfill cells (50 ft square and 20 ft deep). The cut below grade was limited to 9 ft. A sixth cell was completely above ground. The study was conducted over a three year period. The construction of each cell was differed and the initial water content of the refuse varied.

The gases produced in the first five cells consisted chiefly of carbon dioxide and methane. The concentration of methane varied from little more than a trace, in the landfill constructed without the addition of water, to about 50% in the landfill cell whose surface was irrigated with

water. Quantities of hydrogen, up to a maximum of 3.6%, were also detected. The average CH_4 to CO_2 ratios in the different cells varied from 0.03 to 0.9.

Aerobic activity was suspected in the sixth cell where up to 19% oxygen was detected. Amounts of oxygen up to a maximum of 6%, were also detected in the other cells.

It was reported that the production of methane increased considerably after irrigation of the surface of the cell with water.

Stirred - Continuous Digesters

The results from studies by Golueke and McGauhey (17) and Chan and Pearson (10) on the decomposition of cellulosic materials in continuous digesters are summarized in Table 2.

In each case the digester volume used was 3 liters. A constant temperature of 37 ± 1 °C was maintained and the digester contents were continuously stirred with magnetic stirrers. The digesters were fed daily. The theoretical liquid flow through time was 30 days. The results given are average values after steady state conditions were established. The rates calculated from the reported data are on the basis of volatile solids reduction.

The rate constant, k, of reduction of volatile matter varied from 0.007 to 0.014 day^{-1} and appears to vary inversely with the loading of the digesters (lb volatile matter/day - lb volatile matter in digester). Gas production varied from 9.3 to 14 ft^3/lb volatile matter digested. The CH_4 to CO_2 ratio varied from 1.37 to 1.89.

Batch Digesters

The rates of cellulose and total carbon reduction have been calculated from studies by Acharya (18), Stranks (19) and McBee (8), on the digestion of cellulose in batch digesters. The results are summarized in Table 3.

The rates of cellulose reduction varied between 0.0094 and 1.012 day^{-1}. In the studies by McBee (8) a pure strain of cellulolytic bacteria was used which is responsible for the high rates of digestion. The rumen is known to contain many strong cellulose decomposing strains of bacteria (7), and therefore the rate of cellulose decomposition obtained by Stranks (19), who used a rumen fluid culture, is comparable to those obtained by McBee. The rate of cellulose reduction obtained from Acharya's study (18) is very low. However, this may be explained by the fact that the digester was seeded with a culture obtained from rice soil and hence was not acclimatized for cellulose digestion.

The rate of carbon reduction in Acharya's study was 0.0005 day^{-1}. This may be considered as the overall rate constant for the reduction of cellulose to carbon dioxide and methane and is therefore much lower than the rate of cellulose reduction, which is accomplished just by the hydrolysis of cellulose to glucose.

The rate constants for, cellulose reduction in an activated sludge study by Polkowski et al (22), volatile matter reduction in a study on composting by Schulze (23), and carbon reduction in a sanitary landfill (14) were also

calculated.

The rate constants, normalized to 37 °C, for the different studies, including the laboratory experiments (2), are tabulated in Table 4.

The rate constants shown are on three different basis, namely, volatile matter reduction, cellulose reduction and carbon reduction. The rate constants for volatile matter reduction and cellulose reduction are of a similar magnitude, since in all the digestion studies the material digested consisted of approximately 70% cellulose (On a dry weight basis). Essentially these rates are the rate constants for the first stage of decomposition of cellulose, i.e., hydrolysis.

The rate constants for carbon reduction were calculated with the assumption that carbon reduction is due only to the loss by gassification. In any system carbon reduction may also occur due to the loss of intermediate products (volatile acids and alcohols), however, it has been assumed that such losses, if any, were negligible. The carbon reduction rates represent the rate constants for the complete decomposition of cellulosic materials.

As may be observed from Table 4, the maximum rate of cellulose reduction occurs in the case of the activated sludge process and is 1.967 day^{-1}. Comparable rates may be obtained in anaerobic batch digesters when a specific cellulolytic culture is used and efforts are made to optimize digester operation, i.e., control of pH, increased

oppertunity of contact by mixing, and addition of nutrients. The studies by McBee (8) and Stranks (19) are of this type.

In batch digesters using a non-acclimatized culture, very low rates are observed (2,18). Volatile matter reduction rates between 0.007 and 0.014 day^{-1} were reported for stirred - continuous digesters (10,17) and 0.065 day^{-1} for the aerobic composting process (23).

Carbon reduction rates varied from 1.7×10^{-3} day^{-1}, in the case of batch digesters (2) to 3.3×10^{-5} day^{-1}, for sanitary landfills.

The Rate Limiting Step

From the kinetic viewpoint, anaerobic treatment may be described as a three step process involving hydrolysis of complex material, acid production, and methane fermentation. In a complex multi-step process, the kinetics of the slowest step will govern the overall kinetics of waste stabilization. From a study on the kinetics of waste assimilation in anaerobic treatment, McCarty (24) concluded that the rate limiting step in anaerobic waste treatment is the third step, methane fermentation. Lawrence and McCarty (25) studied the kinetics of methane fermentation for different volatile acids in continuous digesters and reported the maximum rates of acetic, propionic, and butyric acid utilization (expressed as an equivalent weight of acetic acid per unit weight of microorganisms) at 8.1, 9.6, and 15.6 mg equivalent acetic acid/mg microorganisms - day, respectively, at 35 °C.

On the basis of volatile acid COD stabilized by conversion of acid to methane, the reported rates are equivalent to 8.7, 7.7, and 8.3 mg acid COD stabilized/mg-day, respectively.

In a recent study on the hydrolysis rate of cellulose, Chan and Pearson (10) reported the maximum rate of hydrolysis of cellulose at 3.21 mg/mg-day or 5.4 mg cellulose COD hydrolyzed/mg-day, and concluded that cellulose hydrolysis is the rate limiting step in the overall decomposition of cellulose under anaerobic conditions.

TABLE 1

THE CH_4/CO_2 RATIO FOE DIFFERENT METHANE FERMENTATION PATHWAYS

Methane Fermentation Pathways, Equations Operative	Case	Gas		%		Ratio $\frac{CH_4}{CO_2}$
		CH_4	CO_2	CH_4	CO_2	
18	A	190	446	29.9	70.1	0.43
	B	120	236	33.7	66.3	0.51
15+18	A	375	631	37.3	62.7	0.59
	B	305	421	42.0	58.0	0.72
14+15+18	A,B	375	631	37.3	62.7	0.59
14+15+16+18	A	502.5	707.5	41.5	58.5	0.71
	B	432.5	497.5	46.5	53.5	0.87
14+15+17+18	A,B	682.5	733.5	48.2	51.8	0.93
14+15+16+17	A	620	1000	38.3	61.7	0.62
	B	690	930	42.6	57.4	0.74
14+15+16+17+18	A,B	810	810	50.0	50.0	1.00

TABLE 2

CONTINUOUS DIGESTER STUDIES

Authors	Reference	Material digested	Time, days	Total Solids %	Loading		% Reduction		Gas		Rate of Volatile Matter Reduction
					lb V_m/ day-ft^3	lb V_m/ day-lb V_m	V_m	Cellulose	Generated ft^3 lb V_m reduced	$\frac{CH_4}{CO_2}$	k day^{-1}
Golueke & McGauhey	17	A	30	2.36	0.154	0.095	65.0	-	14.0	1.38	0.014
"	17	B	30	1.41	0.077	0.165	80.0	91.4	12.1	1.86	0.007
"	17	C	30	2.20	0.077	0.074	67.3	63.5	9.3	1.39	0.013
Chan & Pearson	10	D	30	0.81	0.032	0.136	75.5	93.4	9.8	1.37	0.009

A Dehydrated, ground vegitable trimmings (lettuce, cabbage, etc.).

B 40% Sewage sludge, 60% Paper pulp; 69% Cellulose.

C Synthetic refuse; 10.8% Garbage, 5.5% Grass, 32.9% News paper, 39.5% Kraft paper, 3.9% White fir, and 7.4% Sludge (dry weight).

D Cellulose and Nutrients; 70.6% Cellulose.

V_m Volatile Matter

TABLE 3

BATCH DIGESTER STUDIES

Author		Acharya	Stranks	McBee	
Reference		18	19	8	
Culture		Mixed, from rice soil	Mixed, from rumen	Pure strain of Cellulolytic Bacteria	
Initial Cellulose concentration, %		4.5454	4.12	0.0744	0.298
Time, days		182	3	5	7
Temp. °C		35 to 40	40	55	55
Cellulose * Reduction, %		81.9	84.0	100.0	100.0
Rate Constant at digester temp., day^{-1}	Cellulose Reduction	0.0094	0.59	1.322	1.143
	Carbon Reduction	0.0005	-	-	-
Rate Constant at 37° C, day^{-1}	Cellulose Reduction	0.0094	0.546	1.012	0.875
	Carbon Reduction	0.0005	-	-	-
Remarks		Culture not acclimatized, contents not stirred.	pH maintained at 6.5, end products removed continuously.	-	-

* Assuming that cellulose concentrations below 0.0001% were not detectable.

TABLE 4 *

RATE CONSTANTS FOR DIGESTION OF CELLULOSE AND CELLULOSIC MATERIALS

Process	Culture	Reference	Temperature, °C	Rate Constant, day^{-1} at 37 °C, for the reduction of		
				Volatile Matter	Cellulose	Carbon
Stirred-Continuous Digesters, Anaerobic	Mixed, sewage sludge	10,17	37	0.007 to 0.014		
Batch Digesters, Anaerobic	Mixed, rumen fluid	19	40		0.59	
	Pure * strain	8	55		0.875 to 1.012	
	Mixed, rice soil	18	35 to 40		0.0094	0.0005
	Mixed, varied	2	20 to 55	0.00105 to 0.00216		0.0006 to 0.0017
Activated Sludge, Aerobic	Mixed	22	20		1.475 to 1.967	
Composting, Aerobic	Mixed	23	26 to 63	0.065		
Sanitary Landfill	Mixed	14	16 to 37			3.3×10^{-5}

* A pure strain of cellulolytic bacteria was used

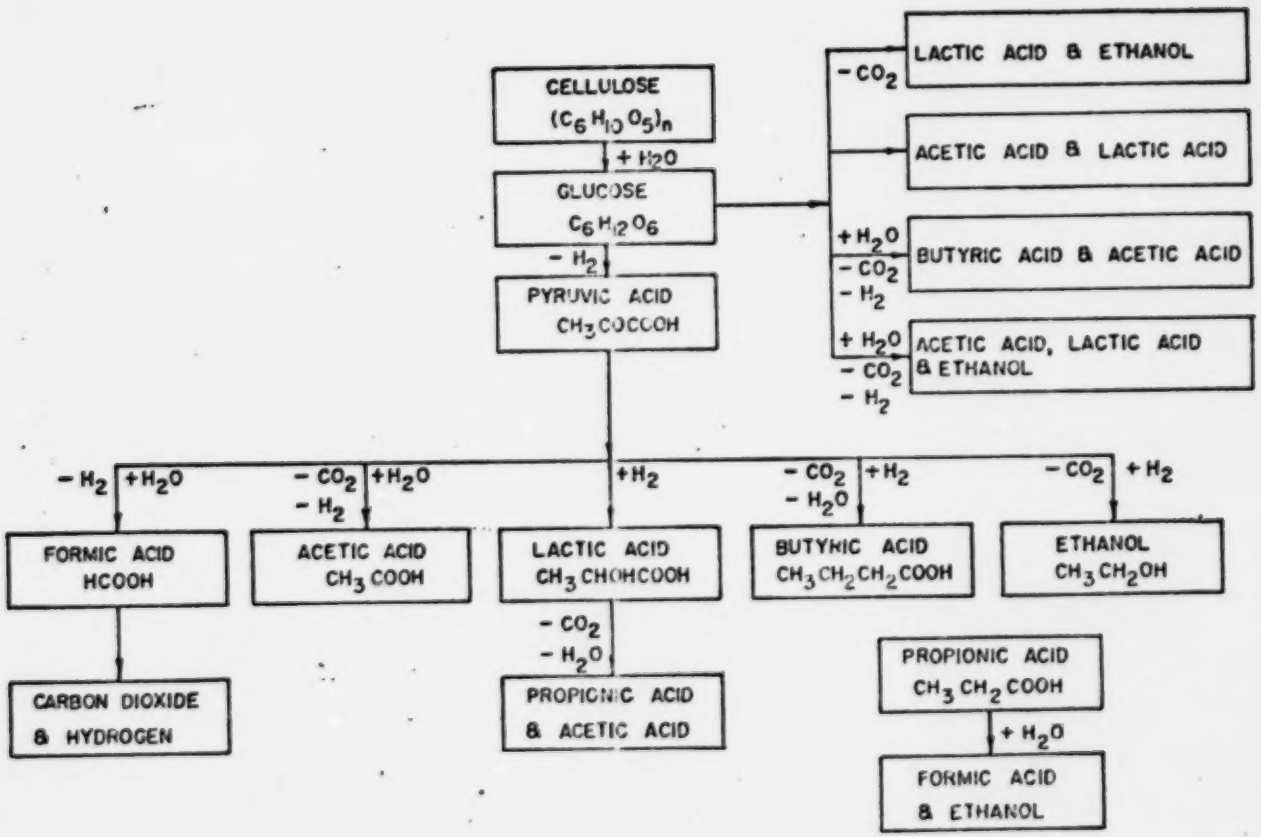

FIG. I. ACID FERMENTATION PATHWAYS

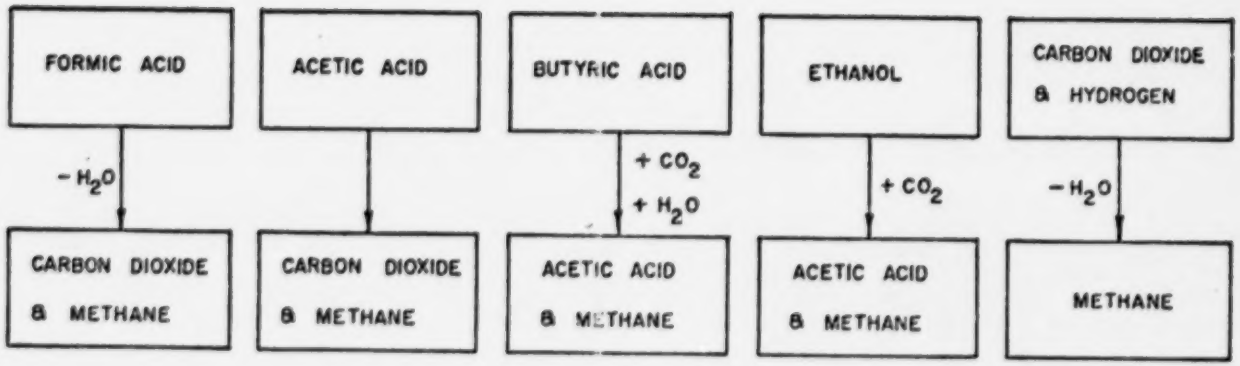

FIG. 2. METHANE FERMENTATION PATHWAYS

ANAEROBIC DIGESTION

The Investigation

A series of batch anaerobic digesters were set up to study the gas production, CH_4 to CO_2 ratio, rates of decomposition and the reduction of volatile matter of milled refuse. Different conditions of seeding, the addition of nutrients and for temperatures ranging between 20 °C and 55 °C were investigated.

A total of six digesters were set up. One digester was at the end of 54 days and the slurry from this digester was used as seed for three of the remaining five digesters, which were in operation for periods ranging from 285 days to 418 days. One digester was not seeded and was operated for 285 days.

Experimental Apparatus

Batch type, anaerobic digestion was carried out in glass containers, 9 to 20 liters in volume. Each digester was provided with a gas collector, a slurry sampling line and a thermometer as shown in Fig. 3. The gases produced were collected in a graduated burette by the displacement of water. Volumes were measured at the temperature of the constant temperature room and one atmospheric pressure. A sampling port was provided in the gas collection line to obtain samples for gas composition analysis. All connections were sealed with General Electric RTV Silicone rubber to

ensure gas tight fits.

Constant temperature was maintained by placing the entire apparatus in a constant temperature room except in the case of the 55 °C digester. In this case, the constant temperature room was maintained at 34 °C and the digester was covered with a thermal jacket, which was necessary for temperature control.

Raw Materials

Milled Refuse

Freshly milled refuse was collected at the milling plant in Madison, Wisconsin, and sealed in 25 lb plastic bags. These bags were stored at 4 °C.

Seed

Activated sludge used to seed digesters No. 1 & 2, was obtained from the Chicago Metropolitan Sanitary District sewage treatment plant in Evanston, Illinois.

The slurry from the seed digester, No. 2, was stored at 4 °C after shut down and used to seed digesters No. 3, 4, & 5.

Water

De-aerated, distilled water was added to the digesters at start up and at subsequent periods to maintain the initial volume of slurry in the digesters.

Nutrients

Nutrients, in the form of $Ca(OH)_2$, $(NH_4)_2SO_4$, K_3PO_4, $Ca_3(PO_4)_2$, and $H_2NC(CH_2OH)_3$, when added to the digesters, were dissolved in water prior to addition.

Experimental Procedures

Digester Operation

Initially digesters No. 1 & 2 were set up at 30 °C. These were seeded with activated sludge and nutrients were added. Digester No. 2, the seed digester, was shut down after a period of 54 days and the slurry from this digester was used to seed digesters No. 3, 4, & 5. The temperatures of these digesters were 34 °C, 20 °C, and 34 °C, respectively. The temperature of digester No. 1 was changed to and maintained at 34 °C after the 54th. day. Nutrients were added to digesters No. 3 & 4, while no nutrients were added to digesten No. 5. Digester No. 6 was operated at 55 °C without the addition of either seed or nutrients.

At start up, samples of milled refuse, ranging in weight from 135 gm to 300 gm, were mixed with water in glass containers and the digestion apparatus was set up in constant temperature rooms. The digesters were seeded and other nutrients were added to it at irregular intervals (see Table 7). Periodically, water was added to the digesters to compensate for losses in slurry volume resulting from samplings for pH and other measurments. The slurry volume in the digesters was maintained approximately constant and ranged from 5 to 11.5 liters, depending on the particular digester.

The characteristics of the Madison milled refuse are given in Table 5 (1). The percent compositions reported are on an as is basis (wet weight).

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Table 6 gives operational data on the time, temperature, weight of milled refuse added, the volume of slurry, and the time gas production commenced, for the different digesters. The different batches (A,B,C, & D) of milled refuse samples are also identified in Table 6.

Table 7 gives the quantities of materials added to the digesters. Time, t_o, for seed addition refers to the day on which the digesters were seeded; and $t_o = 1$ is the day of start up. Nutrients were added at irregular intervals with t_o ranging from 3 to 35 days.

Observations

Initially, the moisture, ash, volatile matter, and carbon contents of the milled refuse were determined. Results of the moisture, ash and volatile matter content tests run on the milled refuse are summarized in Table 8. Results of the ash and volatile matter content of the milled refuse, batch A (digesters No. 1 & 2), are not available and have been assumed to be 35% and 65% respectively for the carbon balance calculations.

Table 9 summarizes the results of the organic and inorganic carbon content of the milled refuse. The average organic and inorganic carbon contents of the milled refuse are 20.1% and 0.74%, respectively. The average total carbon content is 20.85% and was used for the carbon balance calculations.

At shut down, the digester slurry was allowed to settle and the supernatant was decanted off. Total solids

in the settled sludge and the supernatant were determined. The ash, volatile matter and the carbon content of the settled sludge were determined. Tables 10 & 11 summarize the results of the tests on the digested slurry after shut down. No tests were run on the slurry from the seed digester (No. 2), since the slurry was stored for use as seed for later digesters.

During the course of digestion, the gas production and the pH of the digester slurry were measured daily during the initial period; and at longer intervals later as gas production decreased. The digester gas was also analyzed for methane, carbon dioxide, and oxygen irregularly.

The oxygen content of the digester gas are given in Table 12. The time, t, is given in days; and t = 1 refers to the first day of gas production. A maximum oxygen content of 3% was observed from which it may be concluded that leakages of atmospheric air into the system was small.

The results from the gas production, pH of the digester slurry, and the analysis for methane and carbon dioxide are shown in Figs. 4 through 19 and are discussed in Chapter IV.

Analytical Methods

Organic and Inorganic Carbon Contents

The carbon test used was developed by Allison (26) and was modified by Grass and Lemert (27) and Orozco (28). Basically the method consists of the oxydation of the carbon in the sample to carbon dioxide by boiling a mixture of the

sample and an oxydizing agent. The carbon dioxide liberated is measured gravimetrically by absorbtion in a Nesbitt bulb. Chromic acid was used as the oxidizing agent for the organic carbon test while the acid reagent, (H_2SO_4, $FeSO_4 \cdot 7H_2O$ and H_2O) was used for the inorganic carbon test. Mikohbite (NaOH absorbed on an expanded mica base) was used to absorb the carbon dioxide.

pH

A Fisher Titrimeter, model 35 (Fisher Scientific, Pittsburg, Pa.),,was used to determine the pH of the digester slurry. Approximately 75 to 100 ml of slurry was withdrawn from the digester after shaking the digester manually, and the pH measured. The slurry was then returned to the digesters. For digesters No. 1 & 2, the slurry was not returned to the digesters for the first 31 days. For the purpose of carbon balance calculations, it was assumed that 85 ml of slurry was withdrawn for each observation.

Oxygen Analysis

A galvanic cell, oxygen electrode (Precision Scientific Instruments, Chicago, Ill.) was used to determine the oxygen content of the digester gas.

Gas Composition

The gases produced by the digesters were analyzed for methane and carbon dioxide by gas - solid chromatography, using a F & M, Model 300 gas chromatograph (F & M Scientific Corporation of Wilmington, Del.).

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This system uses an adsorption column and a thermal conductivity detecter cell. The column used in this study was 15 ft by 1/8 in I. D. coiled copper tube, packed with 50 to 80 mesh Type Q Porapac (Varian Aerograph, Walnut Creek, CA.). During the study, the column was operated at room temperature (23 °C) with helium as carrier gas. A flow rate of 88 ml/min at a pressure of 72 psig was used.

Gas samples to be analyzed were collected by direct extraction from the gas sampling port, using a 2.5 ml gas-tight syringe (29)

Moisture, Ash, Volatile Matter, and Total Solids

Determinations were made in accordance with the procedures outlined in Standard Methods (30).

Calculations

Standard procedures were adopted to make the gas production, decomposition rates, and the carbon balance calculations. Assumptions made and other details have been discussed where necessary.

TABLE 5

MILLED REFUSE CHARACTERISTICS

Component	Percent by Weight
Food Waste	15.3
Garden Waste	13.8
Paper Products	42.4
Plastics, Rubber, Leather	1.8
Textiles	1.6
Wood	1.1
Metals	6.7
Glass and Ceramics	10.1
Rock, Dirt, Ashes	7.2

The percentages reported are on an as is basis (wet weight), for milled refuse, Madison, Wisconsin, (1971). (1)

TABLE 6

DIGESTER OPERATIONAL DATA

Digester No.	1	2	3	4	5	6
Milled Refuse Sample	A	A	B	B	C	D
Temperature, ° C	30 to 5/25/71 34 hence	30	34	20	34	55
Date started	4/1/71	4/1/71	5/25/71	5/25/71	7/21/71	8/12/71
Date shut down	5/23/72	5/25/71	5/23/72	5/23/72	5/23/72	5/23/72
No. of days in operation	418	54	364	364	307	285
Wt. of Milled Refuse added, gm.	300.0	135.0	225.5	222.0	225.0	225.0
Volume of slurry, l	11.5	6.0	5.5	5.0	6.0	6.0
* Date of gas production	4/3/71	4/4/71	5/26/71	5/27/71	7/24/71	8/25/71
** Δt_o	2	3	1	2	3	13

* First day after initiation on which gas production was more than 20 ml.

** Number of days after initiation.

TABLE 7

MATERIALS ADDED TO DIGESTERS

Digester No.		1	2	3	4	5	6
Wt. of Milled Refuse added, gm.		300.0	135.0	225.5	222.0	225.0	225.0
Seed	Volume, ml.	200(a)	150(a)	150(b)	150(b)	100(b)	0
	Time, t_o, added, days	3	3	1	1	1	-
Wt. of chemicals added, gm. (c)							
$Ca(OH)_2$		20.85	4.67	2.50	3.0	0	0
$(NH_4)_2SO_4$		13.0	2.5	5.25	5.25	0	0
K_3PO_4		1.0	0.25	0.5	0.5	0	0
$Ca_3(PO_4)_2$		0.25	0	0	0	0	0
$H_2NC(CH_2OH)_3$		0	86.0	0	0	0	0
Total		35.1	93.42	8.25	8.75	0	0

(a) Activated sludge

(b) Slurry from digester No. 2

(c) Added at irregular intervals, time, t_o, ranging from 3 to 35 days.

TABLE 8

MILLED REFUSE - MOISTURE AND ASH CONTENT

Milled Refuse Sample	Date Obtained	Moisture Content			Ash Content			Volatile Matter	
		Test date	%	Avg. %	Test date	%	Avg. %	%	Avg. %
A	1/14/71	4/2/71	24.2 20.3 22.4	22.3	-	-	-	-	-
B	5/12/71	5/26/71	20.4 29.6 28.5 27.3	26.5	7/16/71	34.0 37.8	35.9	66.0 62.2	64.1
C	5/12/71	7/22/71	26.4 28.4	27.4	8/14/71	34.8	34.8	65.2	65.2
D	5/12/71	8/12/71	27.0 25.8	26.4	8/15/71	35.9	35.9	64.1	64.1
E	1/2/72	2/10/72 2/11/72 2/14/72 2/16/72 5/24/72	21.3 19.7 20.8 23.2 24.1	21.8	2/28/72 5/24/72	32.1 30.3	31.2	67.9 69.7	68.8

$$\text{Moisture Content} = \frac{\text{Weight of water in sample}}{\text{Weight of sample}} \times 100\ \%$$

TABLE 9

MILLED REFUSE - CARBON CONTENT

Test No.	Type of Test	Carbon, %	Average Carbon, %
1	Organic	23.13	20.11
2		24.07	
3		17.70	
4		24.18	
5		17.00	
6		17.34	
7		18.30	
8		19.20	
1	Inorganic	0.84	0.74
2		0.62	
3		0.71	
4		0.74	
5		0.82	
6		0.68	
7		0.81	
8		0.73	

Average Total Carbon Content = 20.85%

TABLE 10

SOLIDS CONTENT AFTER DIGESTION

Digester No.	Total volume of slurry, ml	Total solids in concentrated sludge, gm.	Total solids in supernatent, gm.	Total solids after digestion, gm.
1	9900	162.3	13.0	175.3
3	4800	136.9	7.2	144.1
4	5500	152.2	8.3	160.5
5	5700	122.7	5.9	128.6
6	5800	103.5	4.7	108.2

TABLE 11

CARBON AND ASH CONTENTS OF DIGESTED SLURRY

Digester No.	% Carbon			% Ash	% Volatile matter
	Organic	Inorganic	Total		
1	5.64	1.31	6.95	42.4	57.6
3	11.94	0.70	12.64	64.9	35.1
4	18.90	0.53	19.43	57.6	42.4
5	15.61	0.99	16.60	54.8	45.2
6	15.00	0.41	15.41	40.3	59.7

TABLE 12

OXYGEN IN DIGESTER GAS

Digester No.	Oxygen in digester gas, %	Time, t, days
1	3.0	91
	1.5	127
3	0.25	30
	1.75	38
4	2.0	37
	1.2	-
5	0.3	-
	0.6	-
6	0.3	-
	0.5	-

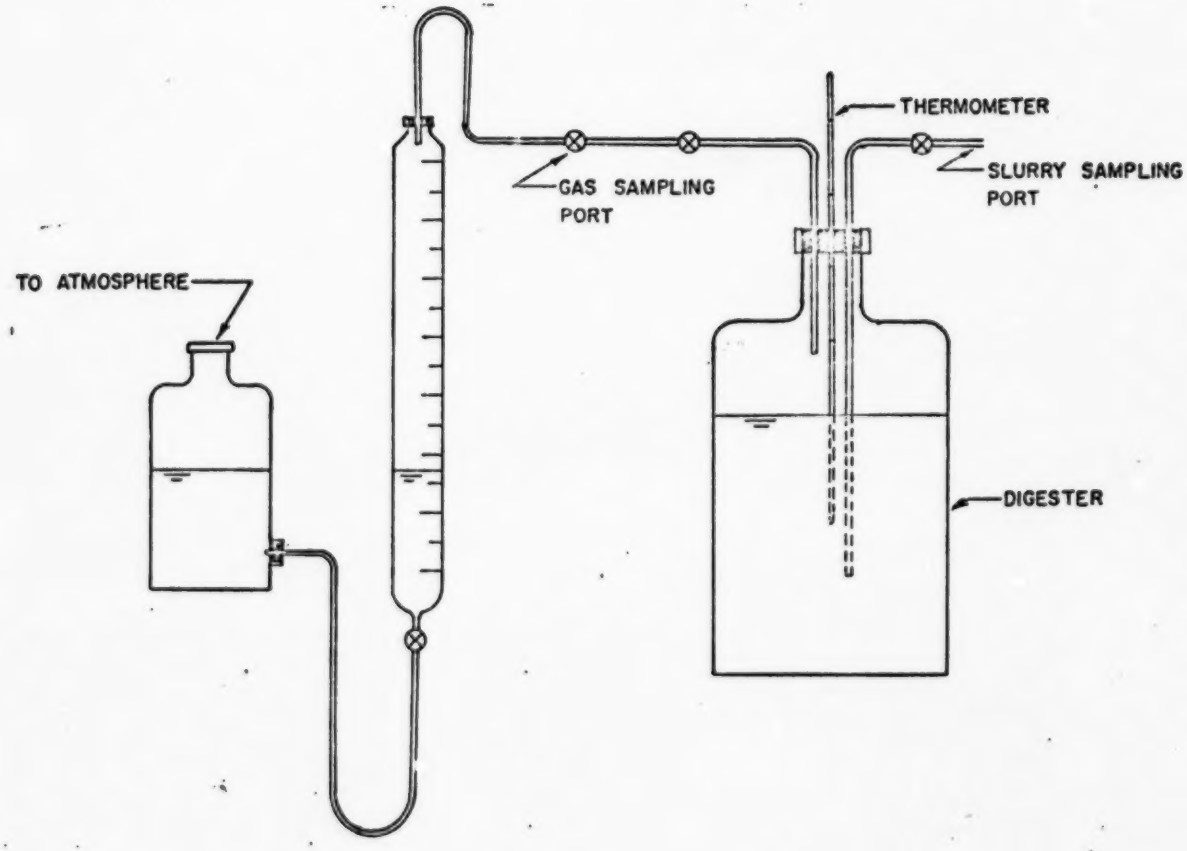


FIG. 3. SCHEMATIC DIAGRAM OF ANAEROBIC DIGESTION APPARATUS

EXPERIMENTAL RESULTS AND DISCUSSIONS

Degree of Digestion

The total solids and the volatile matter reductions in digesters No. 1, 3, 4, 5, and 6, are summarized in Table 13. The maximum total solids reduction of 39.9% was obtained in digester No. 1 and the minimum reduction of 7.0% in digester No. 4. A maximum of 52.4% reduction of volatile matter was obtained in digester No. 3, while the minimum reduction of 33.4% was obtained in digester No. 1.

Gas Production

The average gas production rates for digesters No. 1, 2, 3, 4, 5, and 6 are shown in Figs. 4, 7, 9, 12, 15, and 18, respectively. The time coincides with the actual number of days of gas production; and t = 1 is the first day of gas production. The gas volumes are reduced to 0 °C and one atmospheric pressure. Generally nine day averages are used when daily gas productions were available. The average gas productions are for longer periods during the terminal stages of digestion.

The gas production rates fluctuate considerably. The maximum average rate occurs between t = 28 days and t = 72 days. The maximum nine day average observed was for digester No. 3, for the period t = 64 to 72 days, and was 2080 ml/day. In all the digesters, except the seed digester No. 2, the average gas production rates decreased suddenly

after an initial period of relatively high rates. After this initial period, the average gas production rates decline steadly to approximately 25 ml/day at shut down. This initial period varied from 36 days for digester No. 6, to 117 days, for digester No. 1.

Gas produced by the digesters per pound of total solids, volatile matter, and carbon reduced are shown in Table 14. Digester No. 1 produced 38.7 ft^3/lb of volatile matter reduced. This number is very high as compared to values obtained in other studies as shown in Table 3. Synthetic refuse, similar in composition to the milled refuse, produced 9.3 ft^3/lb of volatile matter reduced in a study by Golueke and McGauhey (17). Theoretically, pure cellulose would produce 13.3 ft^3/lb, if the cellulose were to be transformed completely to carbon dioxide and methane. Thus, the 38.7 ft^3/lb of volatile matter reduced in digester No. 1 is much greater than what may be expected. This suggests an experimental error.

For digester No. 3, 17.7 ft^3/lb of volatile matter reduced was obtained. This is also higher than what may be expected.

Digesters No. 4, 5, and 6 produced, respectively, 12.8, 8.5, and 6.9 ft^3/lb of volatile matter reduced. These values are reasonable, although for digester No. 6, the 6.9 ft^3/lb is on the low side and suggests non-optimal conditions for digestion. This may be the result of not seeding the digester and the fact that no nutrients were

added to this digester.

It may be concluded from the gas production that there is a strong possibility of an experimental error in the case of digesters No. 1 & 3.

pH

The pH of the digester slurry for digesters No 1 to 6 are shown in Figs. 5, 8, 10, 13, 16, and 19, respectively. The time coincides with the actual days of digester operation, that is, $t_o = 1$ at the day of initiation. The days on which the pH values have been shown, have been selected so as to show the fluctuations in pH for the particular digester.

The general trend of the pH seems to be an initial decline after which a fairly steady pH is maintained. The maximum pH observed was 8.4 in digester No. 1 and the minimum, 5.0 in digester No. 5. The average values are between 6.4, for digester No. 5, and 7.2, for digester No. 1.

A pH between 6.6 and 7.6 is generally considered to be optimum for efficient digester performance. The average pH in digester No. 5 was 6.4, which was below the optimum limits. Maintanance of the pH within the optimum limits would probably have caused an increase in the gas production for digester No. 5.

CH_4 to CO_2 Ratio

The CH_4 to CO_2 ratios of the digester gases for digesters No. 1, 3, 4, and 5, are shown in Figs. 6, 11,

14, and 17, respectively. No gas composition tests were made for digester gases from digesters No. 2 & 6, as the gas chromatographic apparatus was not available during the periods of operation of these digesters. The time in these figures corrospond to the actual days of gas production, that is, t = 1 on the first day of gas production.

The average CH_4 to CO_2 ratios for the digester gases from the digesters for the periods of observation are 1.09, 0.58, 0.13, and 0.55, respectively, for digesters No. 1, 3, 4, and 5. These values, however, are not representative since all the observations were within the first 123 days of gas production. From Figs. 5, 10, 13, and 16, an initial drop in pH was observed for the digesters which signifies a build up of volatile fatty acids within the digesters. This indicates that the methane fermentation has not been established. As the microbial population within the digesters get acclimatized, the "methane formers" become more active, that is, the methane content of the digester gases increase or the CH_4 to CO_2 ratio increases.

It may be observed that in the case of digester No. 1, the gas composition analysis were conducted between t = 60 and t = 123 days as compared to between t = 1 and t = 71 days for digesters No. 3, 4, and 5. Consequently, for digester No. 1 the average CH_4 to CO_2 ratio of 1.09 is much higher than those for the other digesters.

The average CH_4 to CO_2 ratio for digester No. 4 is

0.13 which is considerably lower than the ratios obtained for digesters No. 3 & 5. Digesters No. 3 & 5 were operated at 34 °C, while digester No. 4 was operated at 20 °C. This indicates that the "methane formers" are inhibited by low temperatures.

Table 2 shows the CH_4 to CO_2 ratios obtained by other investigators (10,17) on the digestion of cellulosic materials. A ratio between 1.37 and 1.86 was observed for the digesters operating at steady state, that is, when the microbial population was well acclimatized. It will be observed that these values are greater than one, the maximum value predicted for the decomposition of cellulose. However, the CH_4 to CO_2 ratio may be expected to be greater than one for the digestion of cellulosic materials due to the presence of organic materials other than cellulose in the original material to be digested.

Carbon Balance

An attempt has been made to set up a carbon balance for the digesters. However, because of the number of assumptions that had to be made, the carbon balance is far from accurate and may be considered as a rough approximation only.

Table 15 summarizes the calculations to determine the amount of carbon lost from the digester No. 1, by sampling, for the period during which the digester slurry withdrawn for pH measurements were not returned to the digester. The activated sludge, used as seed, was

assumed to have a total solids concentration of 12,000 mg/l, a 65% volatile matter content and a cell composition of $C_5H_7NO_2$. The volume of slurry withdrawn for each pH observation was assumed to be 85 ml. Also, all the carbon lost during a particular day was assumed to have been lost at the end of the day. The estimated amount of carbon lost by slurry sampling for digester No. 1 is 18.69 gm.

Table 16 summarizes the calculations to determine the carbon content of the digester slurry from the seed digester (No. 2). The same assumptions, as in the case of digester No. 1, have been made. The slurry from digester No. 2 was estimated to contain 4.08 gm of carbon per liter of slurry.

The carbon balance is summarized in Table 17. Since no information was available regarding the volatile acids concentration in the digester slurry, it has been assumed that 2,000 mg/l of volatile acids, expressed as acetic acid, was present in the digester slurry at shut down, for all the digesters.

No definite conclusions can be reached from the results because of the approximate nature of the carbon balance. However, it may be observed that for digester No. 1, the carbon lost in the gas exceeds the estimated carbon input. The carbon content of the milled refuse, 62.55 gm, is a reasonable figure, since if it were assumed that the entire volatile matter content of the milled refuse was pure cellulose, we would have a total carbon

content of 67.34 gm. It may therefore be concluded, with a fair degree of certainity, from the carbon balance and the results of the gas production per unit of volatile matter reduced, that the measured volume of gas produced in digester No. 1 was in error and is much greater than what may be expected. Due to the long period of gas production of digester No. 1 (416 days), insignificant errors in the daily gas measurements and the leakage of small amounts of atmospheric air into the system may have accumulated to cause a significant error in the total volume of gas produced.

It may also be concluded, although with a lesser degree of confidence, that the gas volume measured for digester No. 3 was in error. No comments can be made regarding the experimental accuracy for digesters No. 4, 5, and 6 from the information available.

Rate of Digestion

The overall rate constants for the reduction of volatile matter are tabulated in Table 18. From the rate constants, adjusted to 37 °C, it may be observed that the two low rates are for digesters No. 1 & 6. Digester No. 1 was seeded with activated sludge which is not an acclimatized culture for anaerobic digestion and could be responsible for the low rate obtained. The low rate obtained in digester No. 6 may be explained by the absence of seedind and additional nutrients. For digesters No. 3, 4, and 5, the rates obtained are similar and much higher

than those for digesters No. 1 and 6. These digesters were seeded with the slurry from digester No. 2, which may be considered as a fairly well acclimatized culture for the anaerobic digestion of milled refuse and hence the higher rates.

The rate of carbon reduction for the different digesters have also been calculated. It was assumed that carbon reduction is due only to the loss by gassification. For digester No. 1, since the carbon in the gas produced exceeds the estimated carbon input, it was assumed that the initial carbon content was equal to the total carbon recovery, neglecting the losses by sampling (carbon in gas + carbon in digested solids + estimated carbon in volatile acids = 87.57 gm). For comparison, four carbon reduction rates have been calculated for each digester, 1. the overall rate, for the actual days of gas production, 2. the maximum rate, for the nine day period when the maximum average gas production rate was obtained, 3. the initial rate, for the initial period of relatively high gas production, and 4. the terminal rate, for the period following the initial period untill shut down. The carbon reduction rates have been adjusted to 37 ^{o}C. The results are summarized in Table 19.

The overall rates of carbon reduction are significantly higher for digesters No. 1 and 3 as compared to those for digesters No. 4, 5, and 6. This may be expected since it has been concluded that the gas volumes for digesters

No. 1 and 3 were in error.

The rates of carbon reduction and the gas produced per unit weight of volatile matter reduced for digesters No. 1 and 3 have therefore been excluded from the results of the experiment.

The overall rates of carbon reduction are similar for digesters No. 4 and 5 and much lower for digester No. 6, which again may be expected as in the case of the rates of volatile matter reduction.

The rate constants, normalized to 37 ^{o}C, of volatile matter reduction obtained vary from 0.00105 to 0.00216 day^{-1}. Under similar experimental conditions Acharya (18) obtained a rate constant, for cellulose reduction, of 0.0094 day^{-1}. However, purified oat cellulose was used in Acharya's study which is more susceptible to hydrolysis as compared to milled refuse. The overall rate constants of carbon reduction vary from 0.0006 to 0.0017 day^{-1} as compared to 0.0005 day^{-1}, obtained by Acharya. The degree of reduction of the intermideate products (volatile acids and alcohols) in this study (2) is greater than that reported by Acharya. This may be due to the long period of time of digester operation in this study.

TABLE 13

DEGREE OF DIGESTION

Digester No.	1	3	4	5	6
Dry Milled Refuse added, gm	233.1	165.74	163.17	163.35	165.6
Total Solids after digestion, gm (a)	140.20	135.85	151.75	128.60	108.20
Total Milled Refuse Digested gm	92.90	29.89	11.42	34.75	57.40
Digested %	39.9	18.0	7.0	21.3	34.7
Volatile Matter					
Initial, gm	151.52	106.24	104.59	106.50	106.15
After digestion, gm (b)	100.97	50.58	68.05	58.13	64.60
Total digested, gm	50.55	55.66	36.54	48.37	41.55
Total digested, %	33.4	52.5	34.9	45.4	39.1

(a) Exclusive of chemicals added

(b) Correction for chemicals not necessary

TABLE 14

GAS PRODUCTION

Digester No.	1	3	4	5	6
Total Gas Produced @ 0° C & 1 Atms., l	122.21	61.44	29.30	25.66	17.85
Actual Days of Gas Production	416	363	362	304	272
Gas Produced, ft^3/ lb Total Solids Reduced	21.07	32.92	41.09	11.83	8.50
ft^3/ lb Volatile Matter Reduced	38.72	17.68	12.84	8.50	6.88
ft^3/ lb Carbon Reduced *	38.86	34.16	29.30	16.08	9.45

* Calculated on the basis of total carbon removed from the solid phase.

TABLE 15

CARBON BALANCE DIGESTER NO. 1

Day, t_o	Carbon additions	Carbon removals				Total Carbon remaining in digester, gm.
		Samplings, 85 ml		Gas		
		No.	Carbon, gm.	Vol. ml. @ 30° C	Carbon, gm.	
1	300 gm. Milled Refuse; 62.55 gm. Carbon	0	0	0	0	62.55
2	-	0	0	0	0	62.55
3	200 ml. activated sludge; 0.83 gm. Carbon	4	1.85	0	0	61.53
4	-	3	1.36	1035	0.50	59.67
5	-	4	1.76	575	0.28	57.62
6	-	2	0.85	-	-	56.77
7	-	3	1.26	920	0.44	55.07
8	-	1	0.41	410	0.20	54.46
9	-	1	0.40	400	0.19	53.87
10	-	2	0.80	590	0.28	52.80
11	-	4	1.56	960	0.46	50.77
12	-	3	1.13	-	-	49.65
13	-	2	0.73	2350	1.13	47.78
14	-	2	0.71	2440	1.18	45.90
15	-	3	1.02	2420	1.17	43.71
16	-	2	0.65	920	0.44	42.62
17	-	1	0.32	100	0.05	42.26
18	-	1	0.31	1270	0.61	41.34
19	-	1	0.31	690	0.33	40.70
20	-	1	0.30	1100	0.53	39.87
21	-	1	0.29	980	0.47	39.11
22	-	1	0.29	800	0.39	38.43
23	-	1	0.28	600	0.29	37.86
24	-	1	0.28	570	0.28	37.30
25	-	1	0.28	820	0.40	36.62
26	-	1	0.27	870	0.42	35.93
27	-	1	0.27	1350	0.65	35.02
28	-	1	0.26	1320	0.64	34.12
29	-	1	0.25	1250	0.60	33.26
30	-	1	0.25	1110	0.54	32.48
31	-	1	0.24	1620	0.78	31.46

Total Carbon removed by slurry sampling = 18.69 gm

TABLE 16

CARBON BALANCE - DIGESTER NO. 2

Day, t_o	Carbon Additions		Carbon Removals				Total Carbon Remaning in Digester, gm
	Material	Carbon, gm	Samplings, 85 ml		Gas		
			No.	Carbon, gm	Vol., ml @ 30° C	Carbon, gm	
1	135 gm Milled Refuse	28.15	0	0	0	0	28.15
2	80 gm $H_2NC(CH_2OH)_3$	31.74	1	0.39	0	0	59.50
3	150 ml Activated Sludge	0.62	2	1.68	0	0	58.44
4	-	-	2	1.66	248	0.12	56.66
5	-	-	3	2.40	225	0.11	54.14
6	-	-	2	1.54	385	0.19	52.42
7	-	-	2	1.48	680	0.33	50.61
8	-	-	1	0.72	250	0.12	49.77
9	2 gm $H_2NC(CH_2OH)_3$	0.79	1	0.71	240	0.12	49.73
10	-	-	1	0.70	600	0.29	48.74
11	4 gm $H_2NC(CH_2OH)_3$	1.59	1	0.69	150	0.07	49.56
12	-	-	2	1.40	1215	0.59	47.76
13	-	-	2	1.34	900	0.43	45.79
14	-	-	2	1.30	1290	0.62	43.88
15	-	-	2	1.24	670	0.32	42.32
16	-	-	2	1.20	705	0.34	40.78
17	-	-	1	0.58	430	0.21	39.99
18	-	-	1	0.57	530	0.26	39.16
19	-	-	1	0.55	360	0.17	38.44
20	-	-	1	0.54	600	0.29	37.60
21	-	-	1	0.53	480	0.23	36.84
22	-	-	1	0.52	510	0.25	36.07
23	-	-	1	0.51	840	0.41	35.15
24	-	-	1	0.49	710	0.34	34.31
25	-	-	1	0.49	850	0.41	33.41
26	-	-	1	0.47	540	0.26	32.68
27	-	-	1	0.46	890	0.43	31.79
28	-	-	1	0.45	740	0.36	30.98
29	-	-	1	0.44	670	0.32	30.22
30	-	-	1	0.43	530	0.26	29.53
31	-	-	1	0.42	710	0.34	28.77
32 to 54	-	-	0	0	8875	4.28	24.49

Total Carbon in digester slurry at shut down = 24.49 gm.
Volume of digester slurry at shut down = 6 l
Carbon content of digester slurry = 4.08 gm/ l.

TABLE 17

CARBON BALANCE - DIGESTERS NO. 1, 3, 4, 5 & 6

Digester No.	1	3	4	5	6
Wt. of Milled Refuse, gm	300.0	225.5	222.0	225.0	225.0
Carbon in Milled Refuse, %	20.85	20.85	20.85	20.85	20.85
Carbon in Milled Refuse, gm	62.55	47.02	46.29	46.91	46.91
Volume of Seed, ml	200	150	150	100	0
Carbon in Seed, gm	0.83	0.61	0.61	0.41	0
Total Carbon Input, gm	63.38	47.63	46.90	47.32	46.91
Total Volume of Gas @ 0°C & 1 Atms., l	122.21	61.44	29.30	25.66	17.85
Carbon in Gas, gm	65.47	32.91	15.70	13.75	9.56
Total Dry Solids remaining, gm	175.3	144.1	160.5	128.6	108.2
Carbon in Dry Solids, %	6.95	12.64	19.43	16.60	15.41
Carbon in Dry Solids, gm	12.18	18.21	31.19	21.35	16.67
Estimated Carbon in Volatile Acids, gm	7.92	3.84	4.40	4.56	4.64
Total Carbon gm	104.26 *	54.96	51.29	39.66	30.87
Recovery %	166.68	116.89	110.80	84.54	65.81

* Including Carbon removed by slurry sampling (18.69 gm, Table 15)

TABLE 18

RATE CONSTANTS BASED ON VOLATILE MATTER REDUCTION

Digester No.	1	3	4	5	6
Days in Operation	418	364	364	307	285
Temp. ^{o} C	34	34	20	34	55
Volatile Matter Digested, %	33.4	52.4	34.9	45.4	39.1
k day^{-1}, at Temperature of Digestion	0.00097	0.002	0.0012	0.00197	0.00174
k day^{-1}, at 37^{o} C	0.00105	0.00216	0.0019	0.00213	0.00133

TABLE 19

RATE CONSTANTS BASED ON CARBON REDUCTION

Digester No.	Temperature, °C	Period	Time Period, t, days	Rate of Carbon Reduction, k day^{-1}	
				At Digester Temperature	At 37° C
1	34	Overall	1 to 416	0.0035	0.0038
		Maximum	37 to 45	0.0106	0.0115
		Initial	1 to 117	0.0083	0.0089
		Terminal	118 to 416	0.0016	0.0017
3	34	Overall	1 to 363	0.0032	0.0035
		Maximum	64 to 72	0.0447	0.0483
		Initial	1 to 72	0.0119	0.0129
		Terminal	73 to 363	0.0011	0.0012
4	20	Overall	1 to 362	0.0011	0.0017
		Maximum	55 to 63	0.0048	0.0076
		Initial	1 to 117	0.0025	0.0039
		Terminal	118 to 362	0.0005	0.0008
5	34	Overall	1 to 304	0.0011	0.0012
		Maximum	28 to 36	0.0067	0.0072
		Initial	1 to 63	0.0035	0.0038
		Terminal	64 to 304	0.0005	0.00054
6	55	Overall	1 to 272	0.0008	0.0006
		Maximum	28 to 36	0.0062	0.0047
		Initial	1 to 36	0.0053	0.0041
		Terminal	37 to 272	0.0002	0.00015

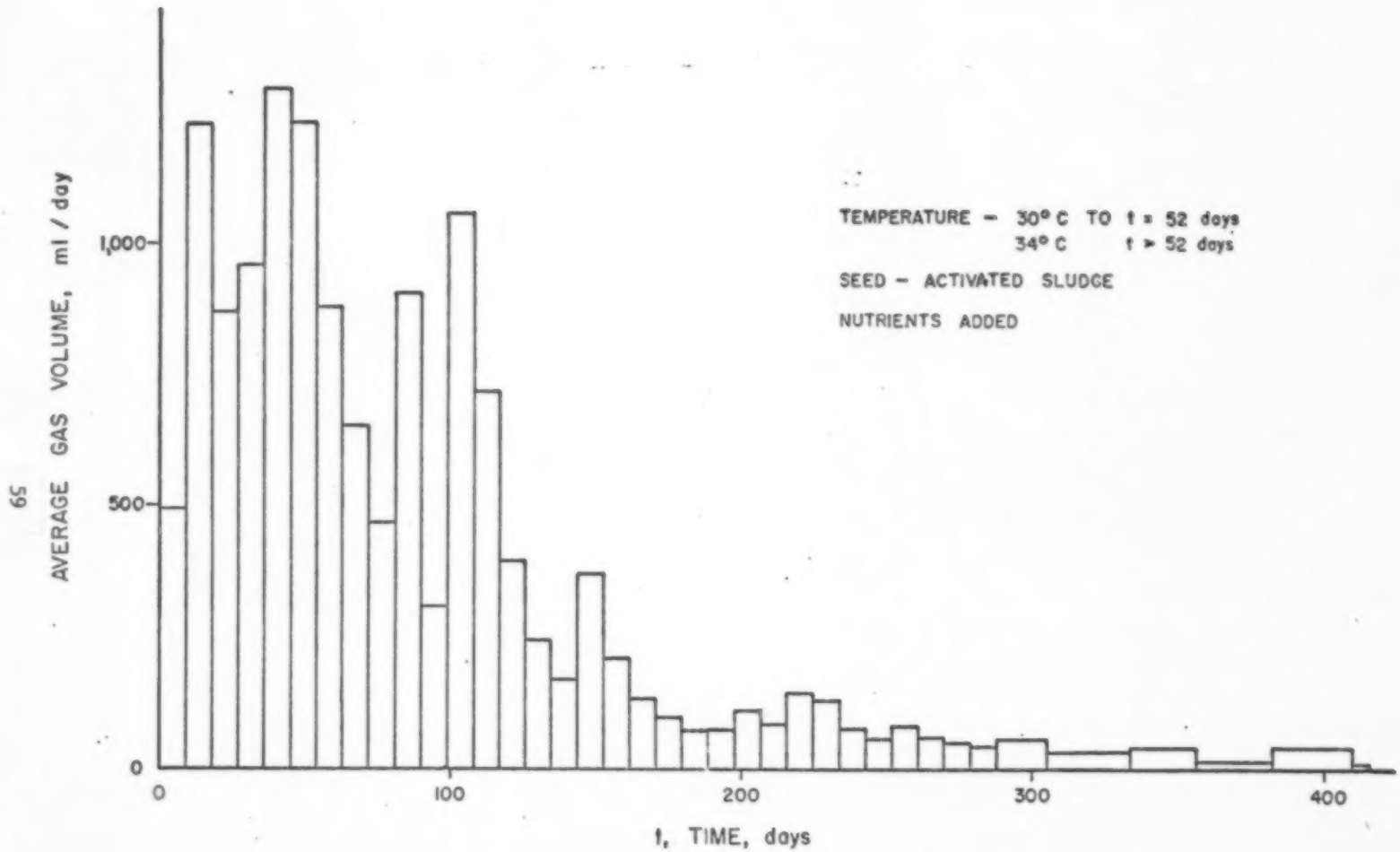


FIG. 4. GAS PRODUCTION vs. TIME – DIGESTER NO. I.

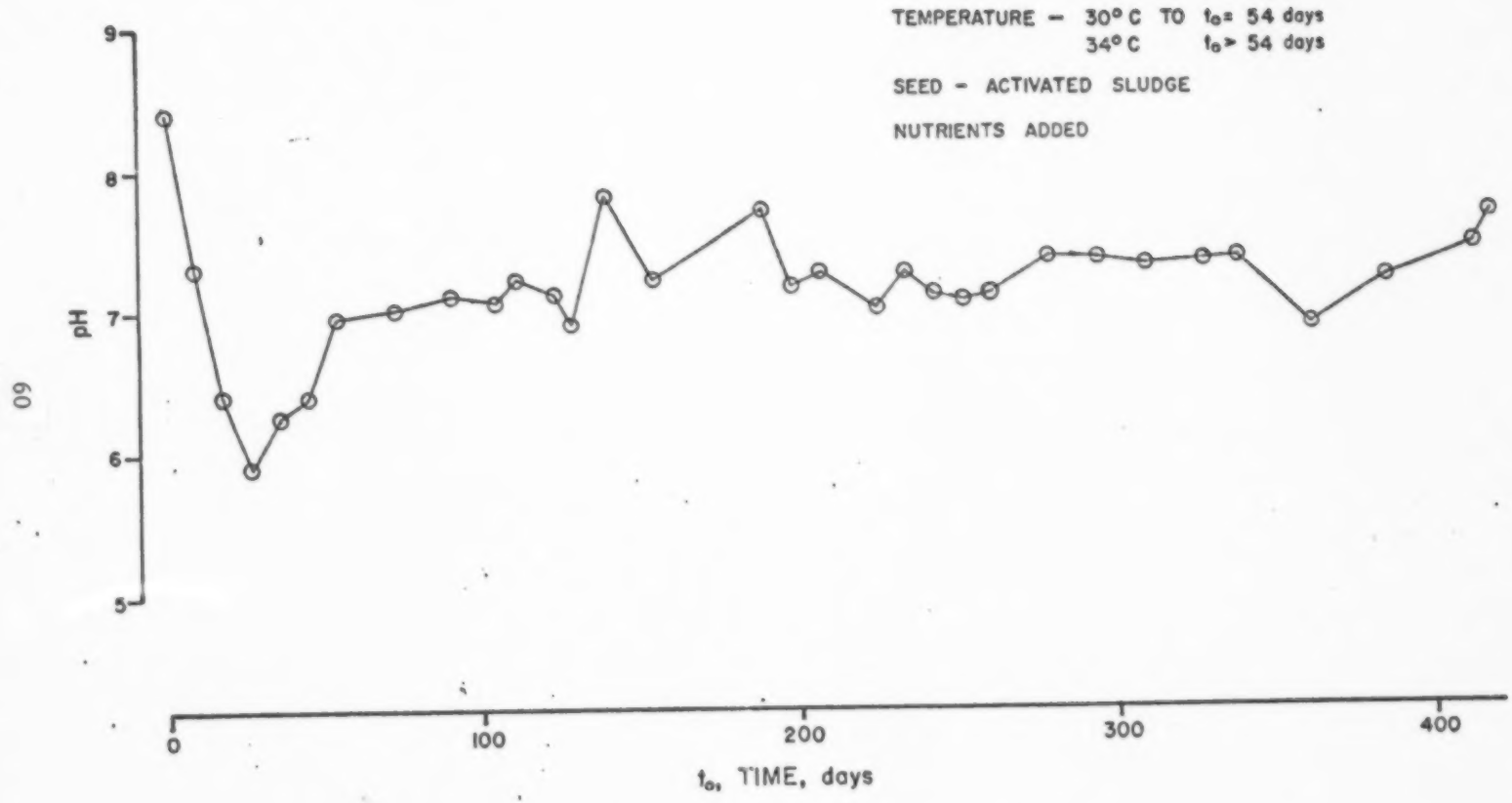
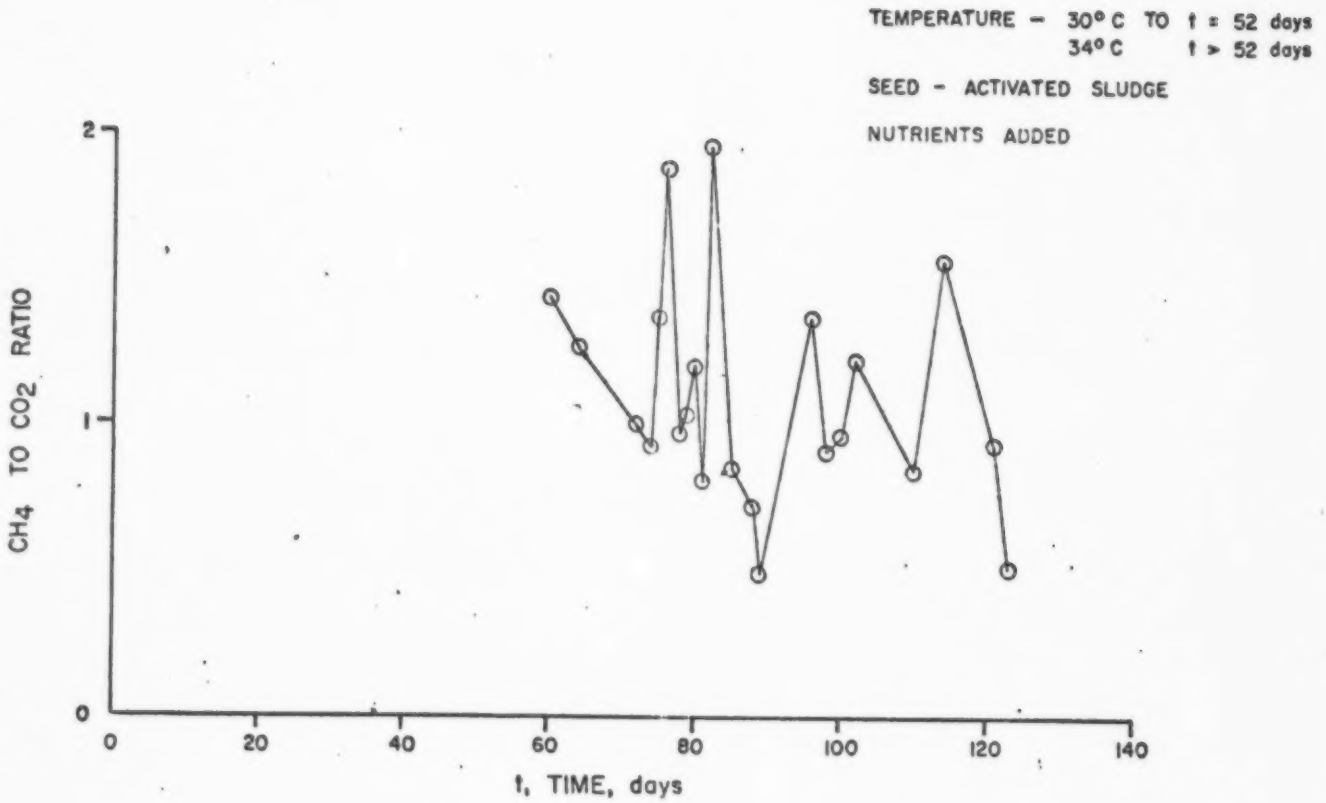


FIG. 5. pH vs. TIME – DIGESTER NO. I.



T9

FIG. 6. CH_4 TO CO_2 RATIO vs. TIME – DIGESTER NO. 1.

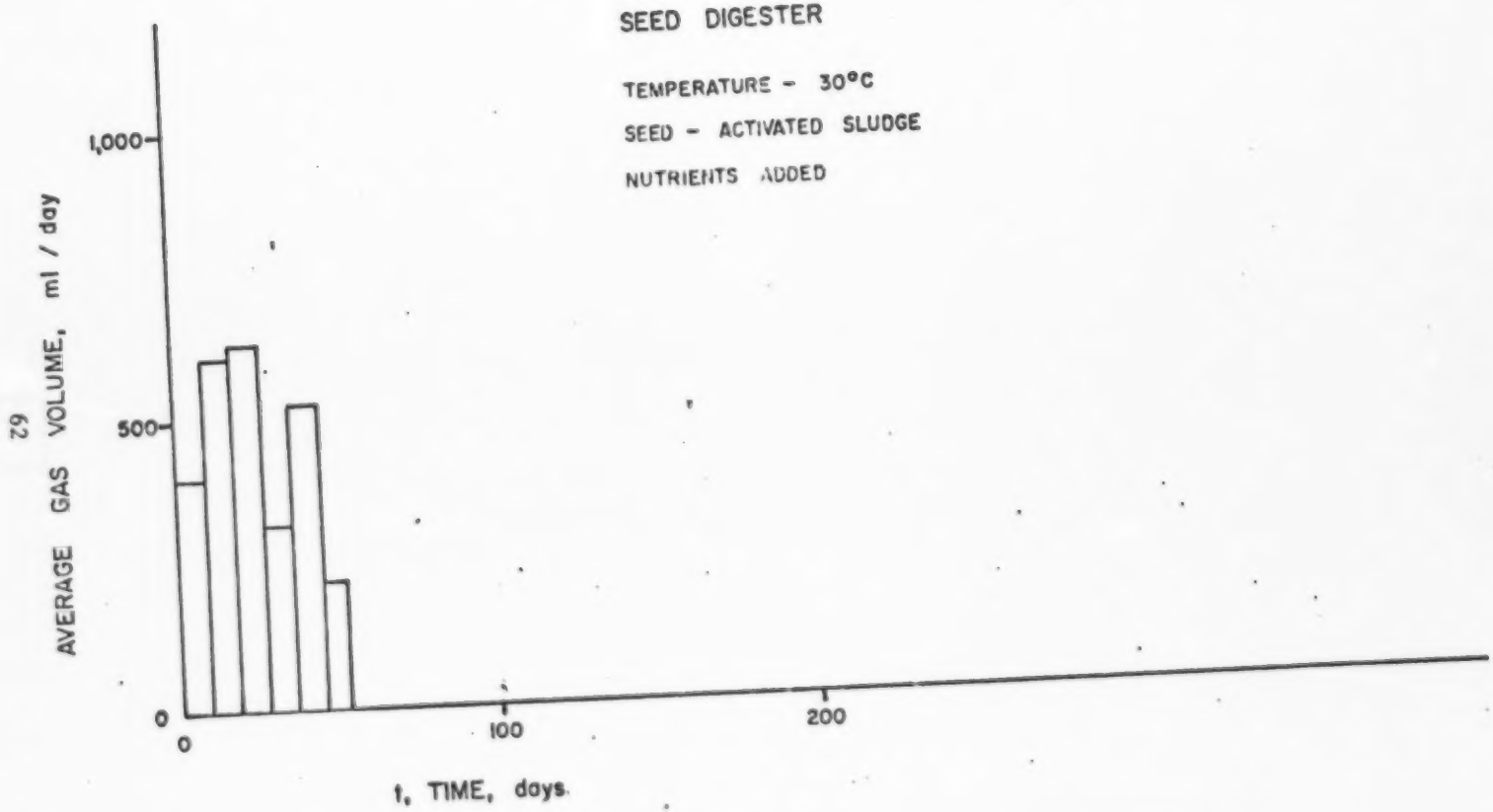


FIG. 7. GAS PRODUCTION vs. TIME - DIGESTER NO. 2.

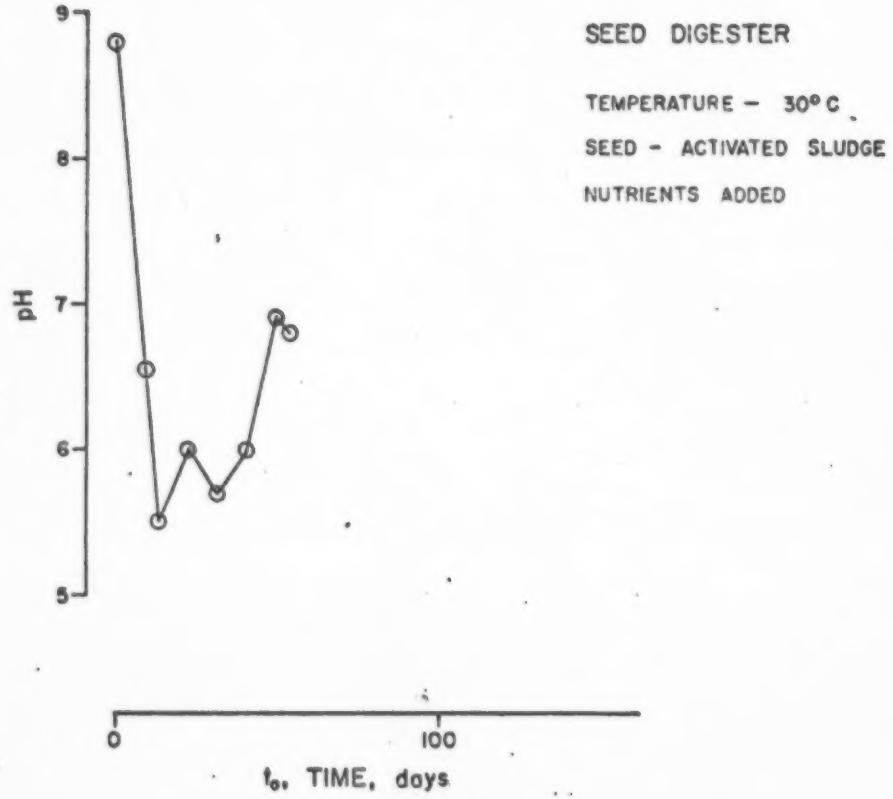


FIG. 8. pH vs. TIME – DIGESTER NO. 2.

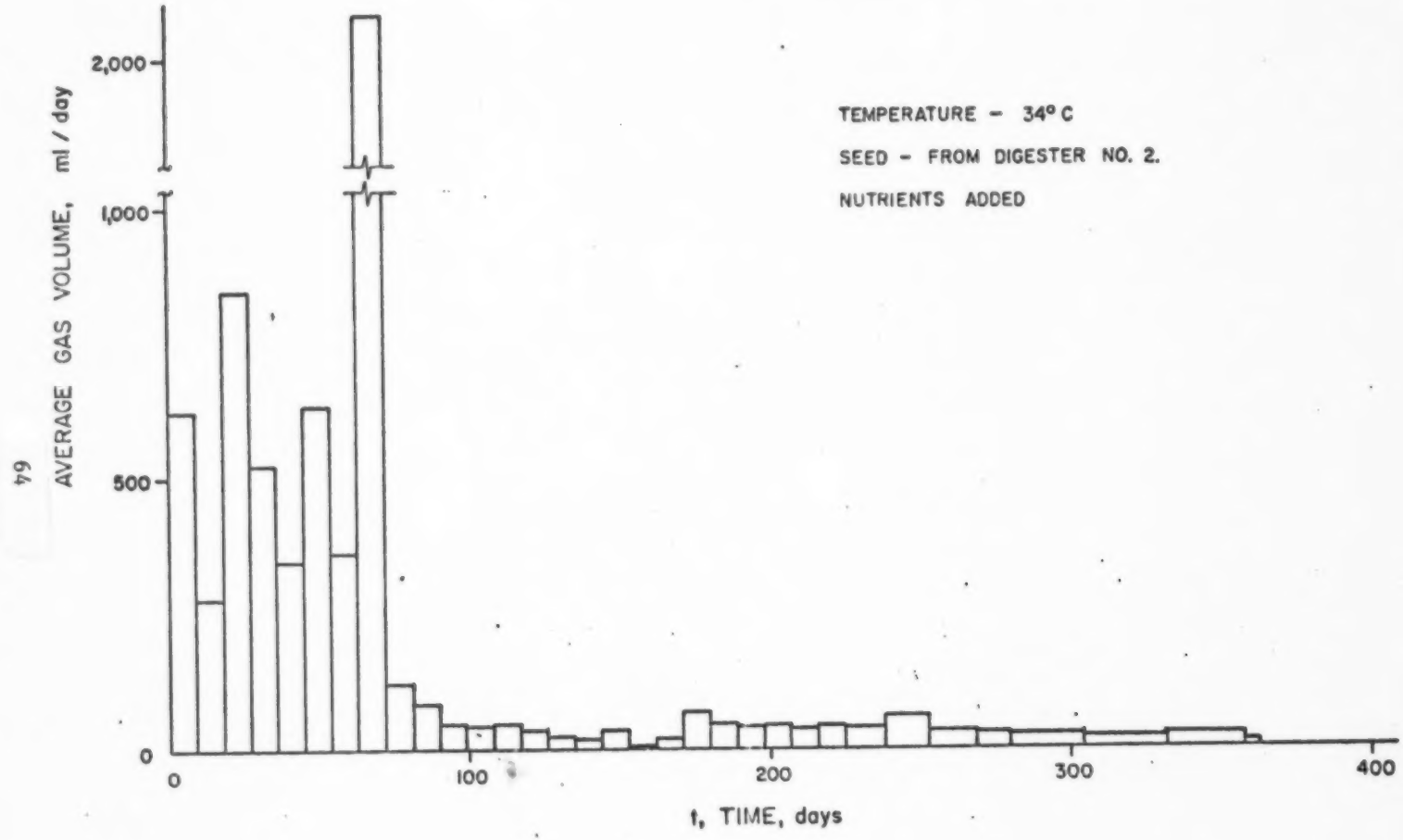


FIG. 9. GAS PRODUCTION vs. TIME — DIGESTER NO. 3.

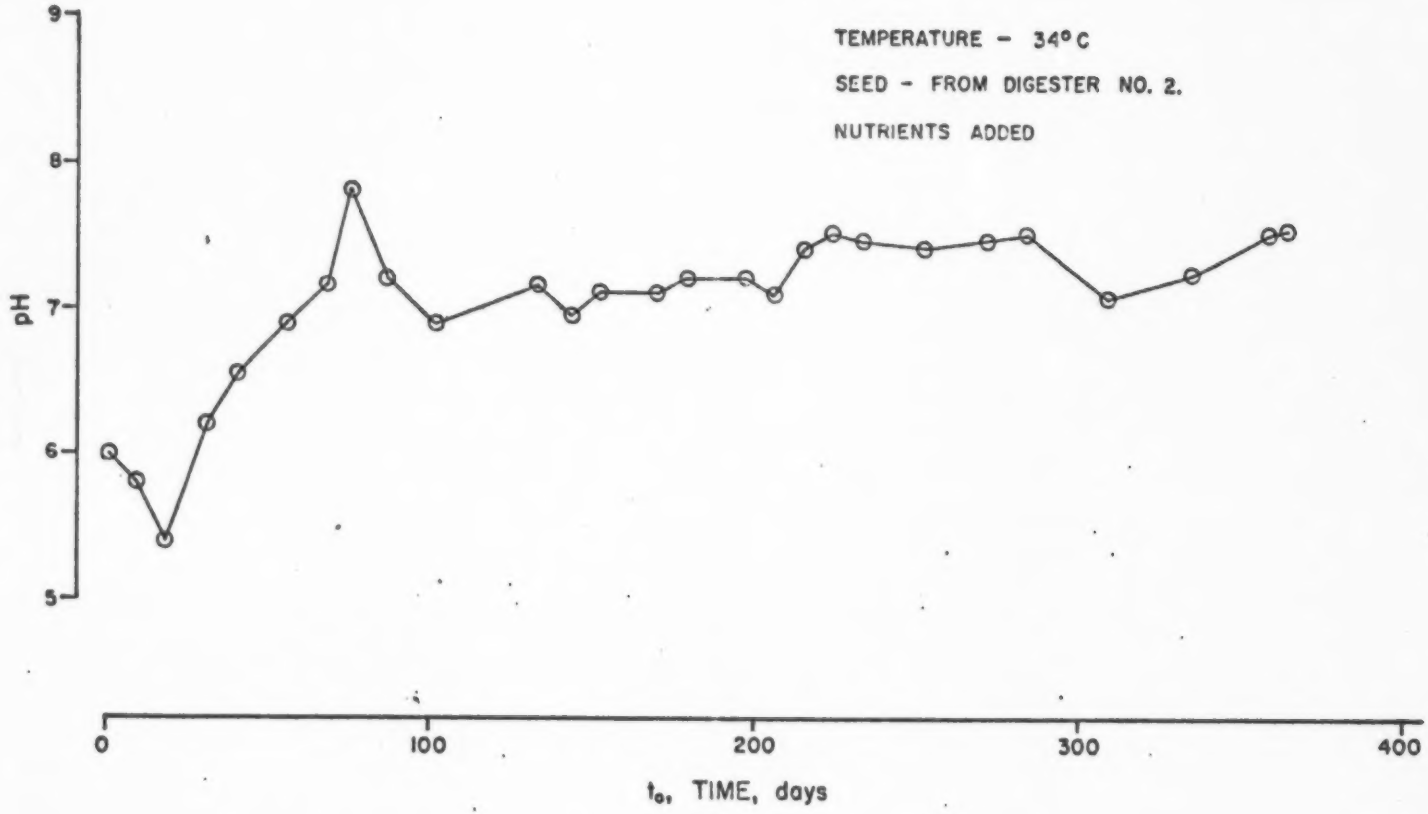


FIG. 10. pH vs. TIME – DIGESTER NO. 3.

TEMPERATURE - 34° C

SEED - FROM DIGESTER NO. 2.

NUTRIENTS ADDED

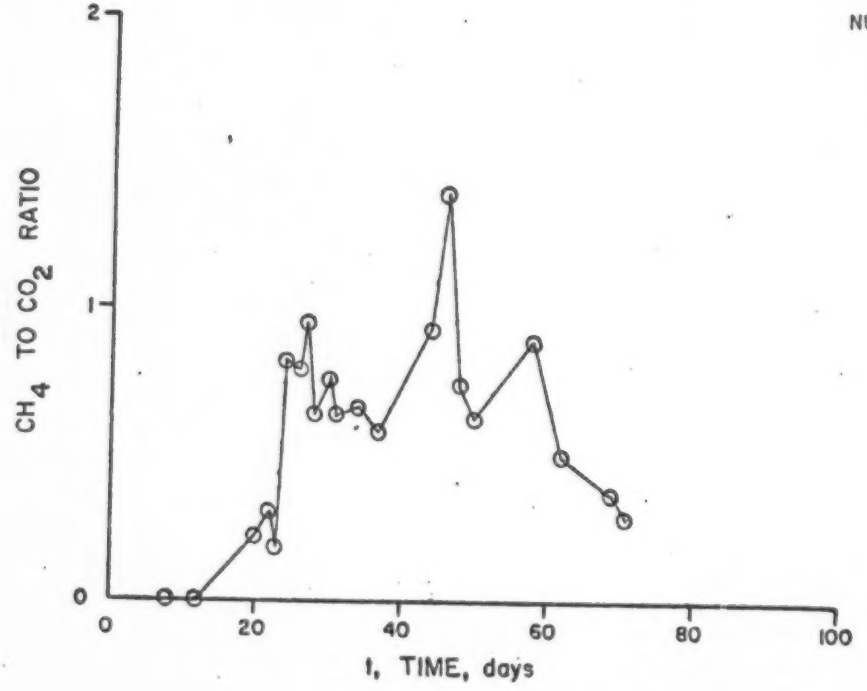


FIG. II. CH_4 TO CO_2 RATIO vs. TIME — DIGESTER NO. 3.

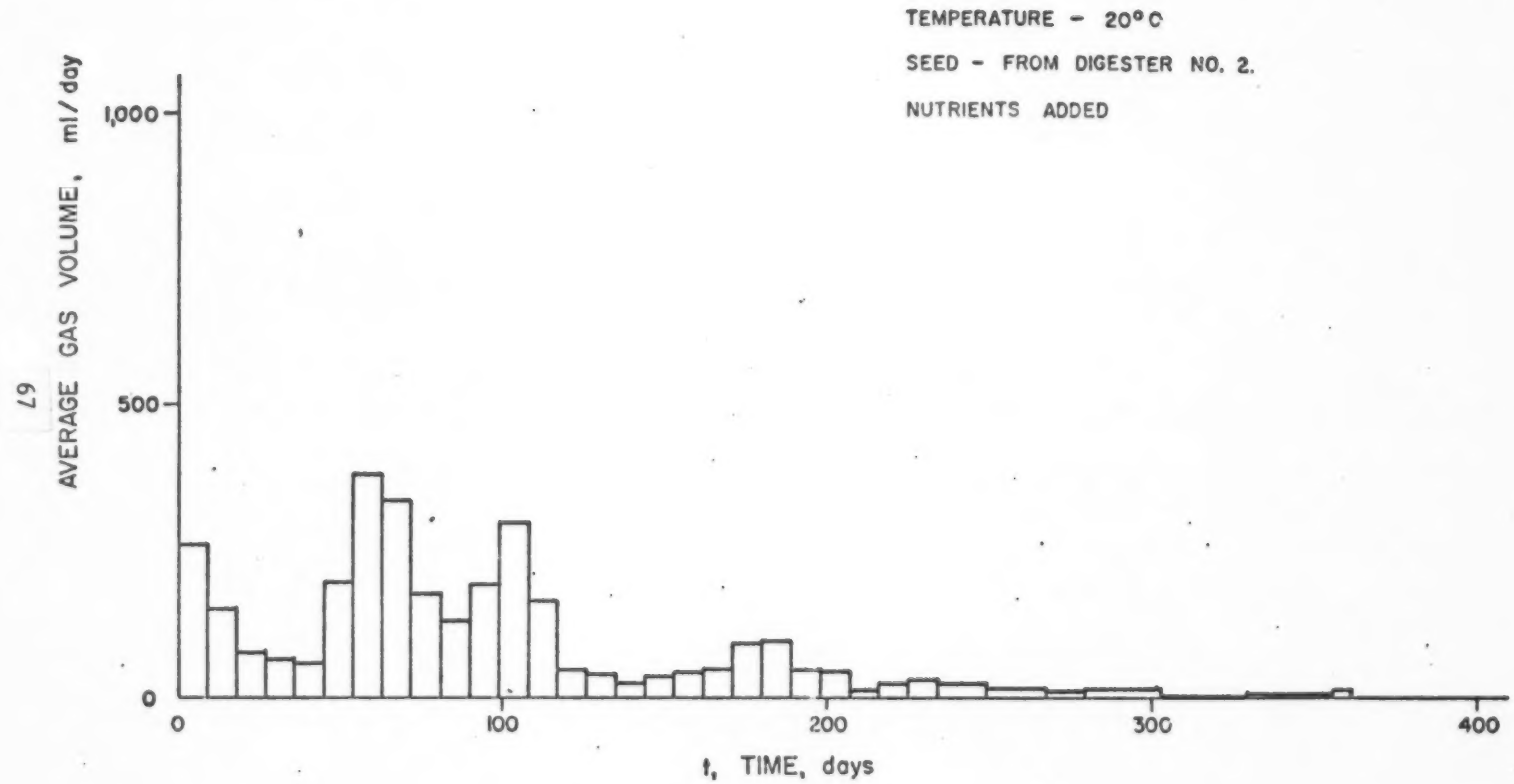


FIG. 12. GAS PRODUCTION vs. TIME – DIGESTER NO. 4.

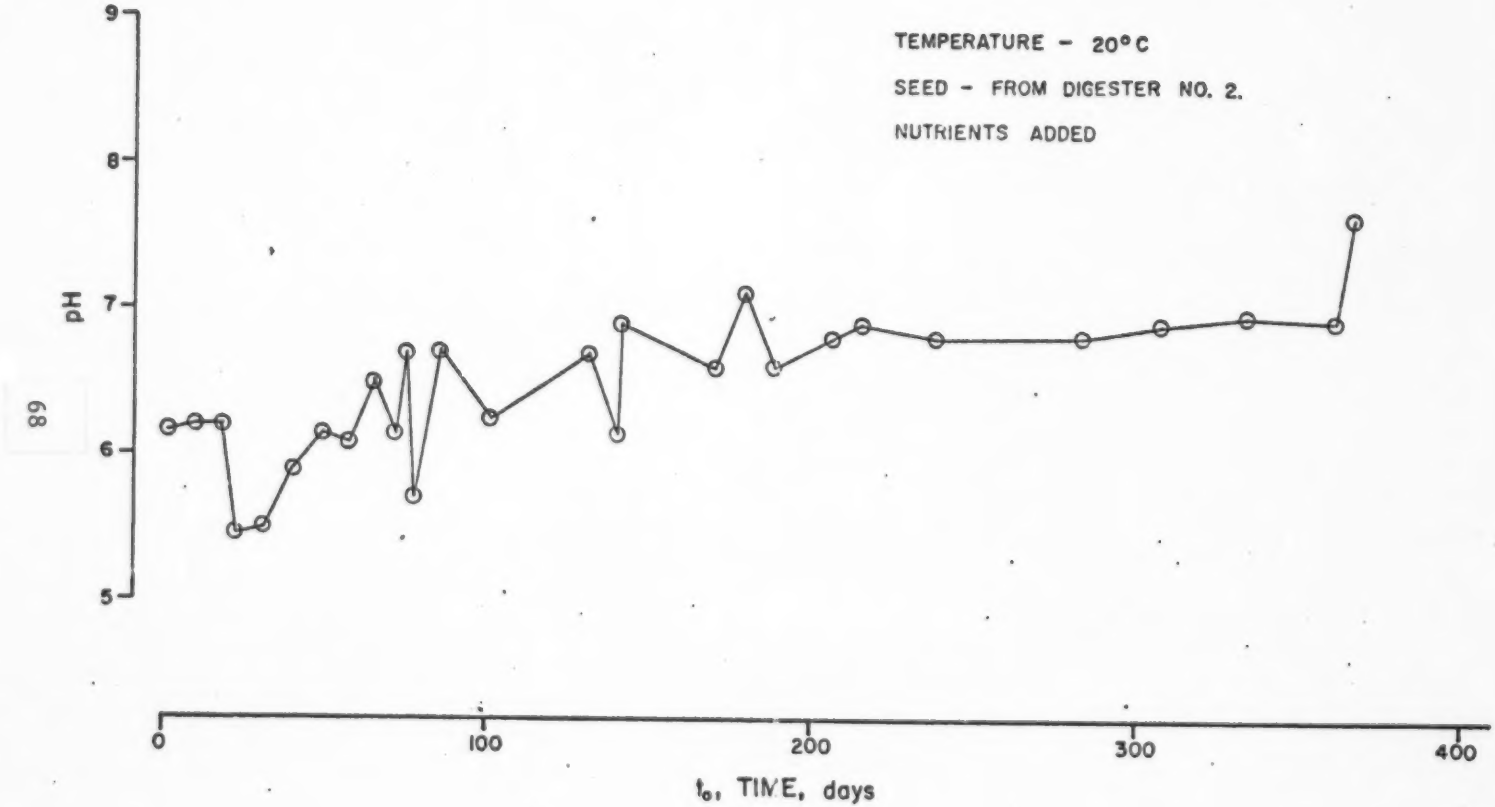


FIG. 13. pH vs. TIME - DIGESTER NO. 4.

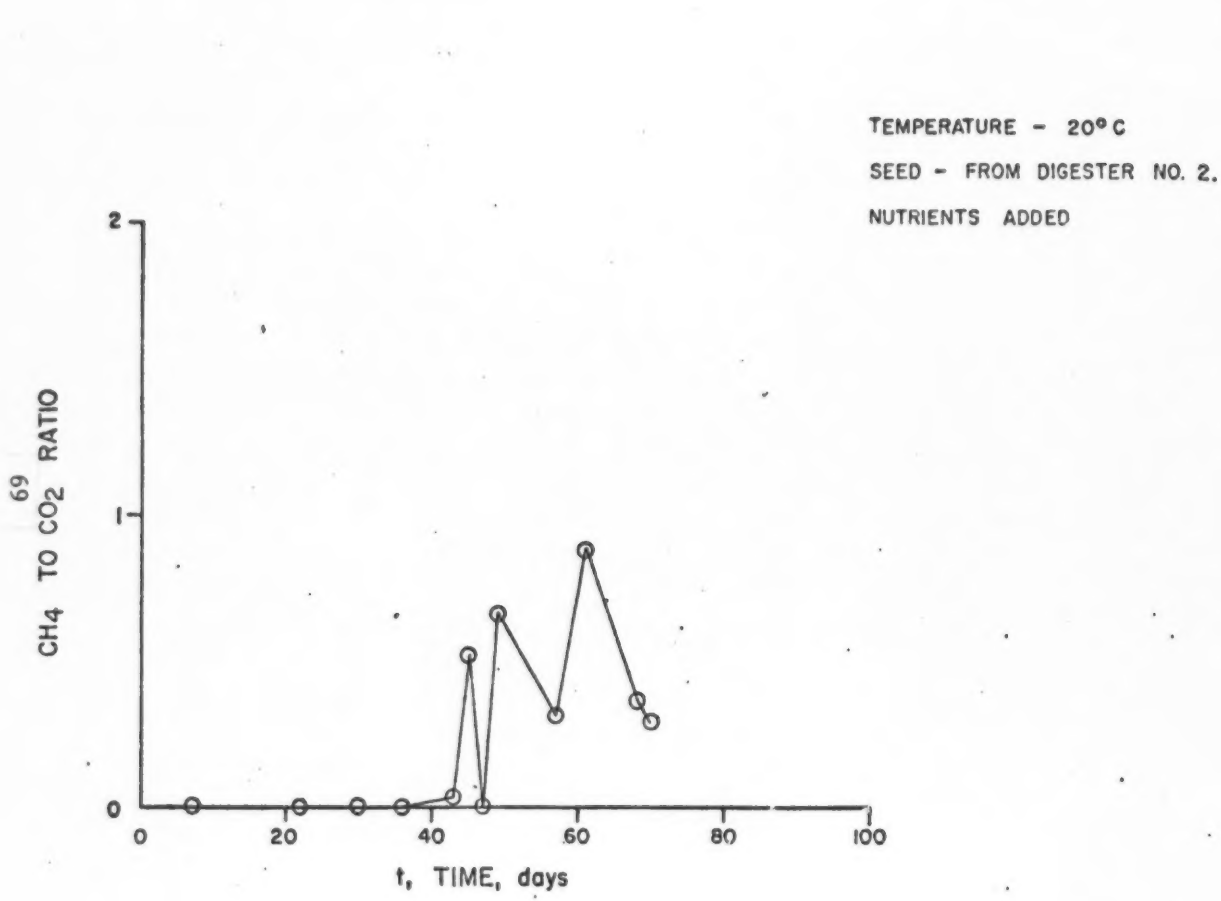


FIG. 14. CH_4 TO CO_2 RATIO vs. TIME – DIGESTER NO. 4.

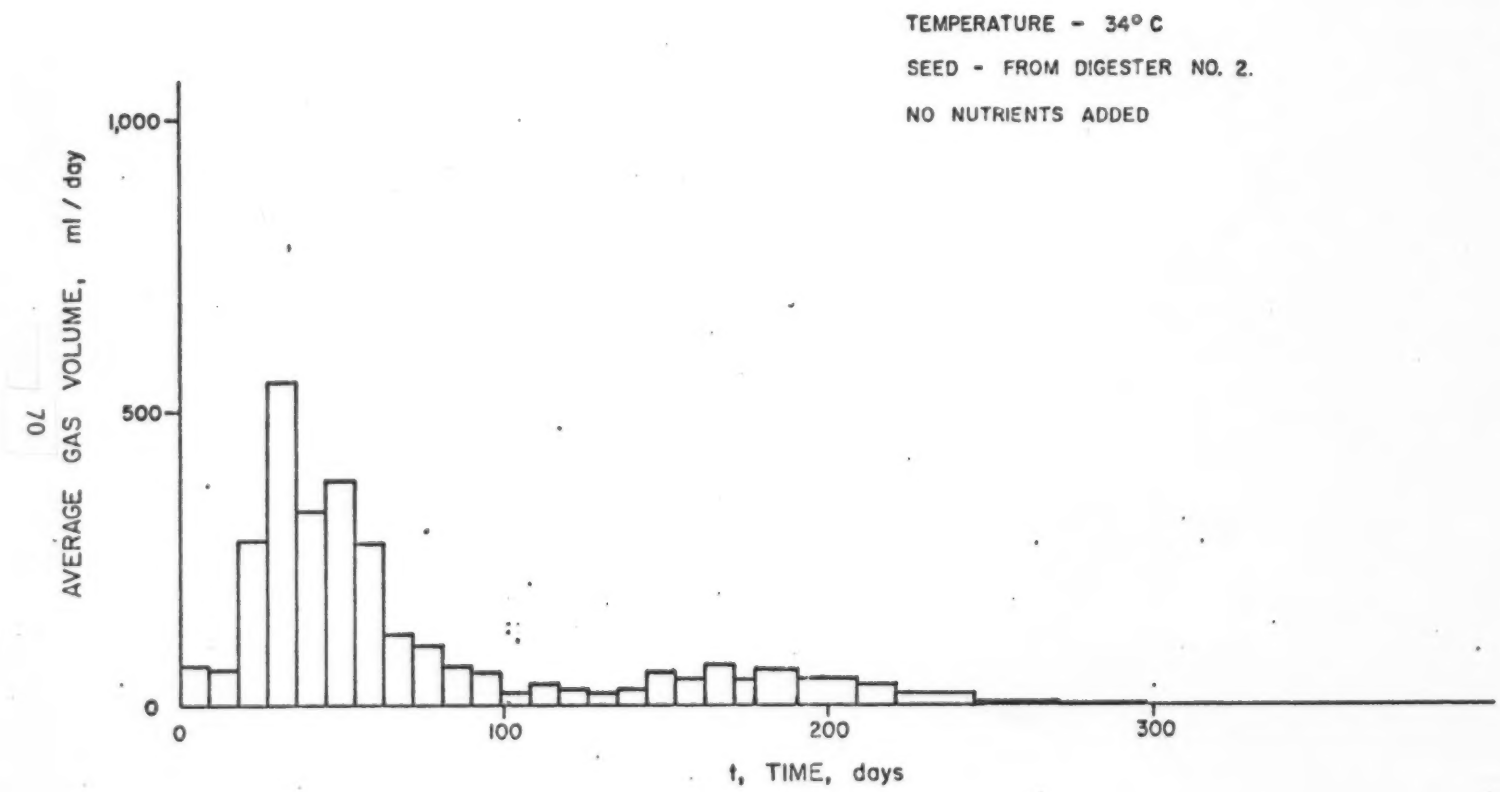


FIG. 15. GAS PRODUCTION vs. TIME – DIGESTER NO. 5.

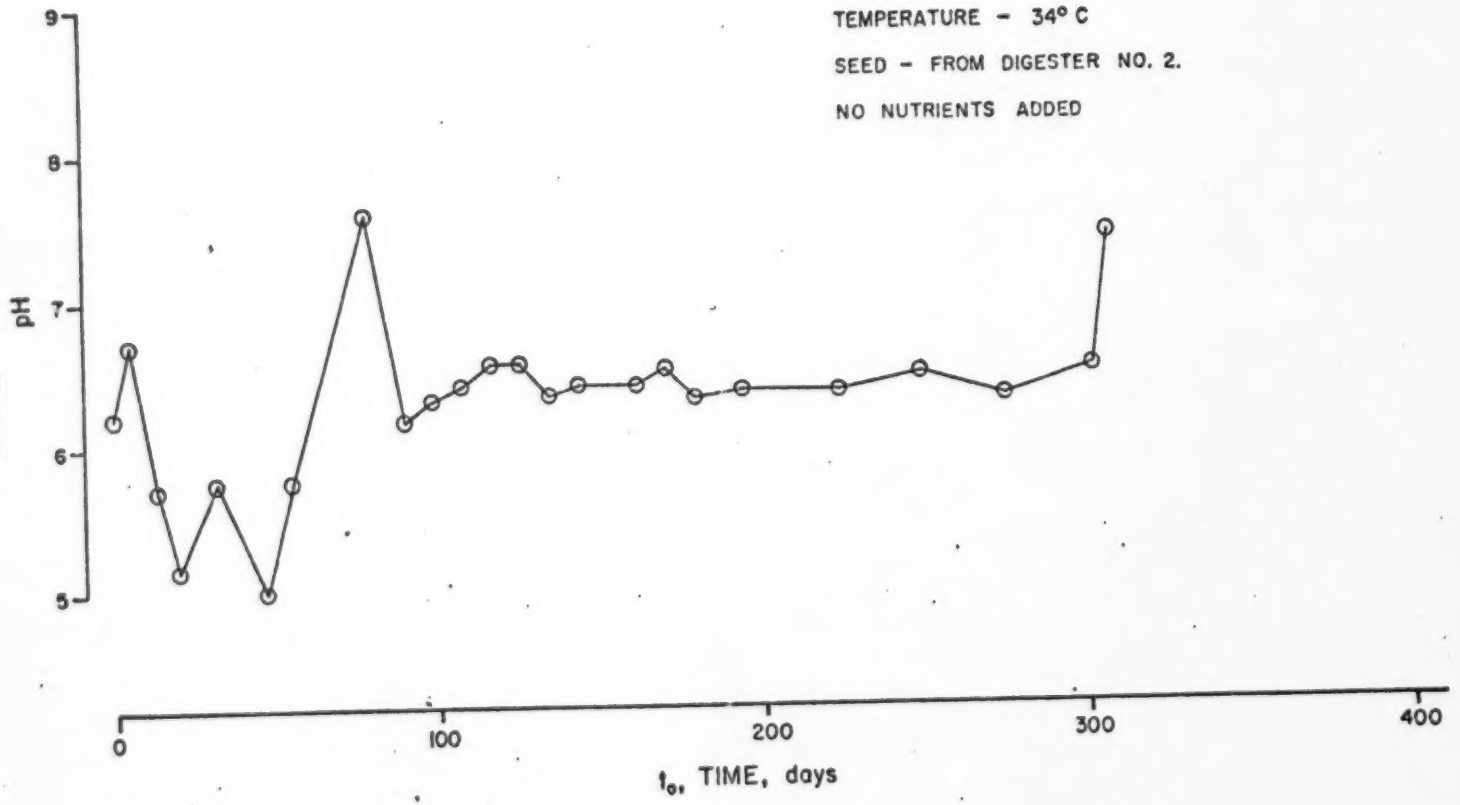


FIG. 16. pH vs. TIME — DIGESTER NO. 5.

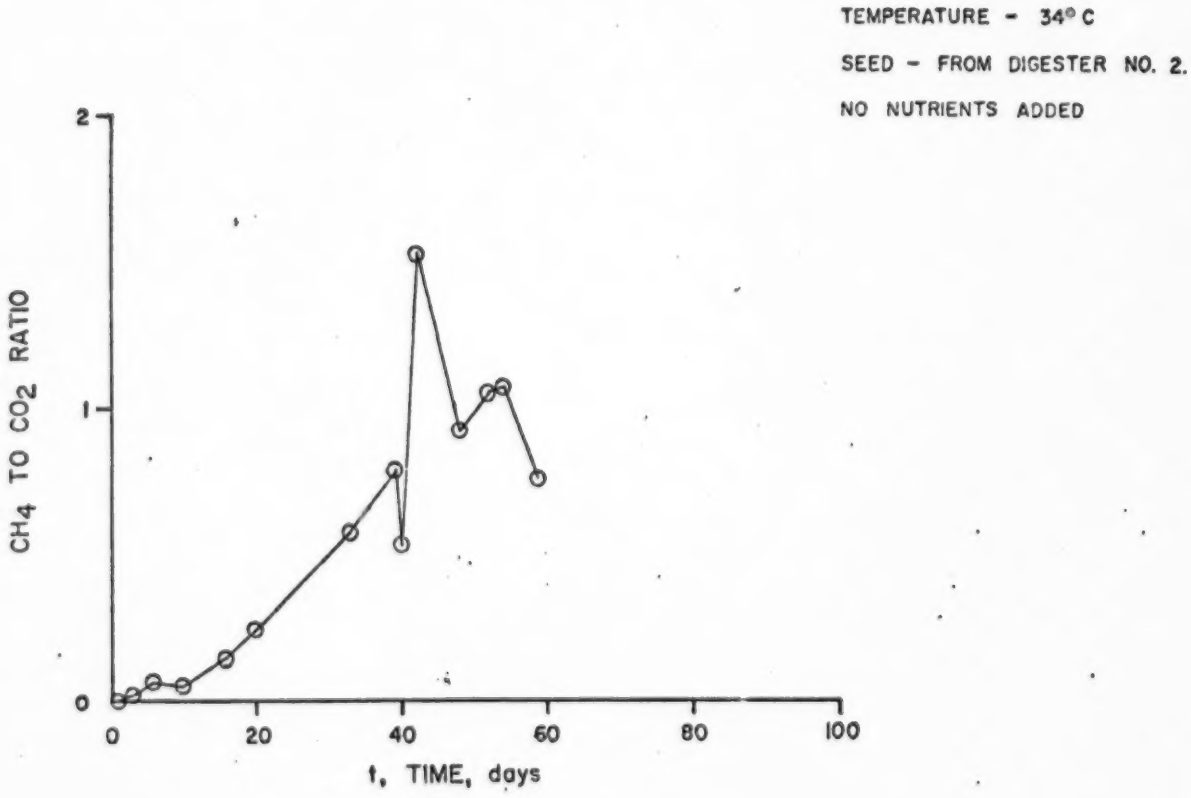


FIG. 17. CH_4 TO CO_2 RATIO vs. TIME – DIGESTER NO. 5.

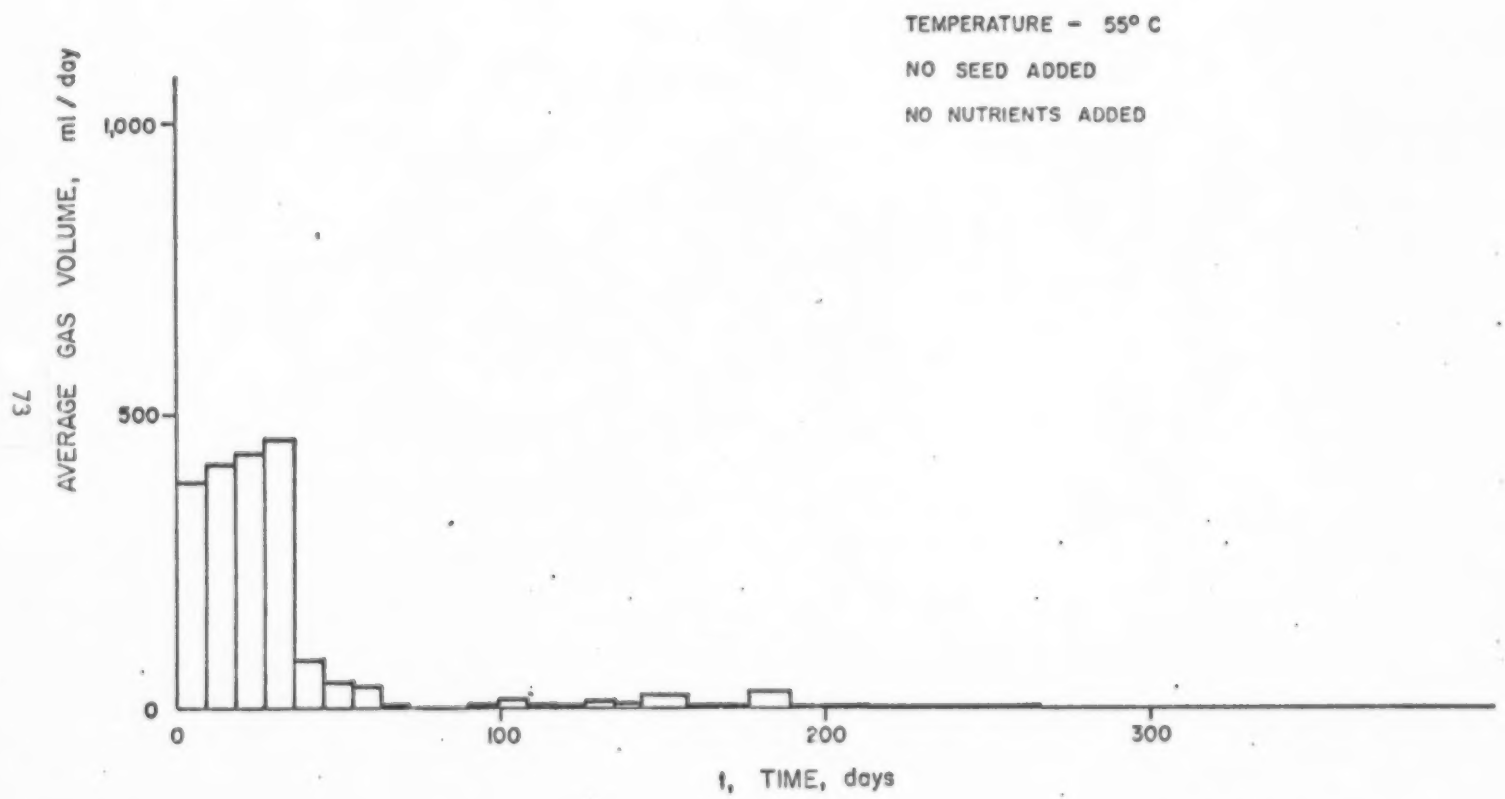


FIG. 18. GAS PRODUCTION vs. TIME — DIGESTER NO. 6.

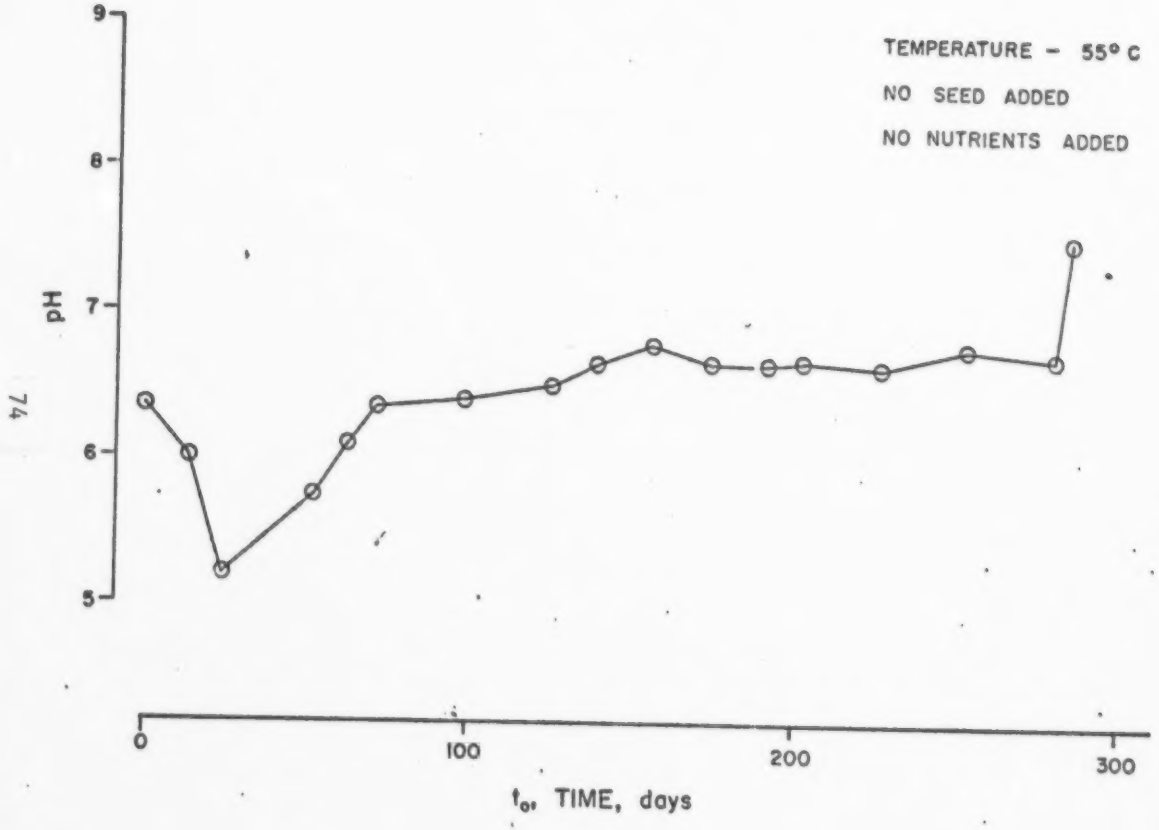


FIG. 19. pH vs. TIME – DIGESTER NO. 6.

SUMMARY AND CONCLUSIONS

This study of the anaerobic decomposition of cellulosic materials was undertaken to provide an understanding of the rates of decomposition, the gas production per unit weight of volatile matter reduced and the CH_4 to CO_2 ratios of the gases produced. A literature search was conducted to obtain the ranges of rates of decomposition, gas production and the CH_4 to CO_2 ratios for similar and different systems. Finally, data from laboratory experiments by Franklin, Zimmerman, and Gupta (2) were analyzed and compared with the information obtained from the literature.

Also, a general scheme for the anaerobic decomposition of cellulose and the overall chemical reaction associated with the scheme is presented.

From the literature search it may be concluded that:

1. The rates of cellulose reduction range from 1.97 day^{-1} for the activated sludge process to 0.0094 day^{-1} for the anaerobic batch digestion of cellulosic material using a non-acclimatized, mixed culture.
2. The rates of carbon reduction in conventional sanitary landfills are extremely low. In one case it was estimated at 3.3×10^{-5} day^{-1} (14).
3. Under favourable conditions, reported gas production in anaerobic decomposition of cellulosic materials

in experimental digesters ranged from 9 to 14 ft^3/lb of volatile matter digested.

4. Gas production in sanitary landfills are low. In two instances experimental landfills (14,15) produced 1.13 and 0.11 ft^3/lb of dry refuse during the first 750 days of operation.

5. For the complete reduction of cellulose, the CH_4/CO_2 ratio may be shown to have a maximum value of one. The ratio may be less than one when, either because all the methane fermentation pathways are not available, or the methane fermentation reactions do not go to completion. However, for the decomposition of cellulosic materials the CH_4/CO_2 is usually higher than one due to the presence of organic compounds other than cellulose in the original material to be digested.

6. The CH_4/CO_2 ratio was reported to vary between 1.37 and 1.86 for experimental digestion of cellulosic materials.

7. In experimental landfills the CH_4/CO_2 ratio was reported to vary between 0.03 and 0.9. The ratio increased with time and with moisture content.

From the analysis of the experimental data of Franklin, et al, (2) it may be concluded that:

1. Seeding of the digester is extremely important. Significant increases were observed in the rate of digestion and gas production when an acclimatized

culture was used rather than a non-acclimatized culture.

2. The overall rate of volatile matter reduction in the digesters ranged from 0.00105 to 0.00216 day^{-1}.
3. The overall rate of carbon reduction in the digesters varied from 0.0006 to 0.0017 day^{-1}. The maximum rate of carbon reduction observed for a nine day period was 0.0076 day^{-1}.
4. The gas production varied from 6.9 to 12.8 ft^3/lb of volatile matter digested.
5. The average CH_4/CO_2 ratio, for the initial phase of gas production, ranged between 0.13 and 1.09, for the different digesters. The ratio was found to increase with time. The CH_4/CO_2 ratio was considerably lower for the digester at 20 ^oC as compared to those at 34 ^oC.

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